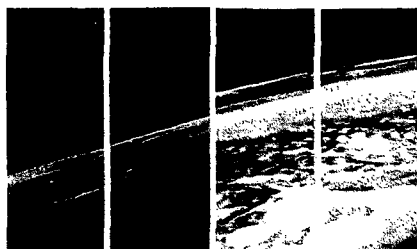


WORKSHOP ON INNOVATIVE INSTRUMENTATION FOR THE IN SITU STUDY OF ATMOSPHERE-SURFACE INTERACTIONS ON MARS



MSATT

Mars Surface and Atmosphere Through Time

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**WORKSHOP ON
INNOVATIVE INSTRUMENTATION FOR THE *IN SITU* STUDY OF
ATMOSPHERE-SURFACE INTERACTIONS ON MARS**

Edited by

Bruce Fegley Jr. and Heinrich Wänke

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PREFACE

This volume contains papers that have been accepted for the MSATT Workshop on Innovative Instrumentation for the *In Situ* Study of Atmosphere-Surface Interaction of Mars, October 8–9, 1992, in Mainz, Germany. The Scientific Organizing Committee consisted of B. Fegley Jr. (Washington University) and H. Wänke (Max-Planck-Institut für Chemie), co-conveners, and L. M. Mukhin (Max-Planck-Institut für Chemie).

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A BACKSCATTER MÖSSBAUER SPECTROMETER (BaMS) FOR USE ON MARS. D. G. Agresti^{1,3}, R. V. Morris², E. L. Wills¹, T. D. Shelfer¹, M. M. Pimper¹, M.-H. Shen¹, and T. Nguyen³,
¹Physics Department, University of Alabama at Birmingham, Birmingham AL 35294, USA, ²Code SN4, Planetary Science Branch, NASA Johnson Space Center, Houston TX 77058, USA, ³Lockheed Engineering and Sciences Co., Houston TX 77058, USA.

Introduction: We have proposed the use of Mössbauer spectroscopy for *in situ* analysis on the surface of Mars [1] and have discussed the design and implementation of a backscatter Mössbauer spectrometer (BaMS) instrument suitable for planetary missions to the surfaces of Mars (MESUR), the Moon (Artemis and lunar outpost), asteroids, or other solid solar system objects [2]. The BaMS instrument is designed to be capable of analysis of a sample for the mineralogy of its iron-bearing phases without any sample preparation.

A requirement of lander missions to Mars is instrumentation for *in situ* mineralogical analyses. Such analyses provide data needed for primary characterization as to the type of surface materials present and by inference the processes that formed and subsequently modified them. For purposes of providing diagnostic information about naturally occurring materials, the element iron is particularly important because it is abundant and multivalent (primarily 0, +2, and +3 oxidation states). Knowledge of the oxidation state of iron and its distribution among iron-bearing mineralogies tightly constrains the types of materials present. The pivotal role of iron was already recognized in 1978 by COMPLEX [3], who recommended development of flight instruments that would identify mineralogy and the oxidation state of iron in planetary surface materials.

The near-term U.S. strategy for the exploration of Mars is the MESUR (Mars Environmental SURvey) program, which entails emplacement of a network of small, long-lived surface landers. For the Moon, BaMS has been recommended as part of a three-instrument landed payload for the Artemis missions, targeted for 1997 [4]. BaMS would prospect for ilmenite, an oxygen resource material, and provide data to assess the maturity of lunar soil. Because instrumental characteristics are low mass, low volume, and low power consumption, BaMS is suitable for implementation on even small landers and rovers, as are being envisioned in MESUR and Artemis concepts. In addition to providing highly diagnostic data, a BaMS analyzer is inherently simple and, as is highly desirable for remote operation, no sample preparation is required.

BaMS Instrument: Basically, a Mössbauer spectrometer consists of a multichannel analyzer, a ⁵⁷Co source (for iron studies) attached to a velocity transducer, and a radiation detector. Backscatter geometry, where the source and detector are on the same side of the sample, will be employed so that no sample preparation is required. For a planetary instrument, several modifications of the transducer and detector components of a typical laboratory instrument are required to minimize mass, power, volume, and time required for a good experiment.

Although we have tested solid-state translators as velocity transducers, the most likely to be implemented relatively quickly is a miniaturized version of the conventional loudspeaker-type design. Our current drive weighs ~20 g, operates at a vibration frequency of ~100 Hz, and requires ~100 mW power [2]. It is rugged and suitable for a planetary BaMS.

Conventional spectrometers generally employ gas-filled proportional counter detectors, and we have designed and tested one as a backscatter detector [2]. However, silicon PIN diodes were introduced as part of a BaMS development for Mars '96 [5]. When

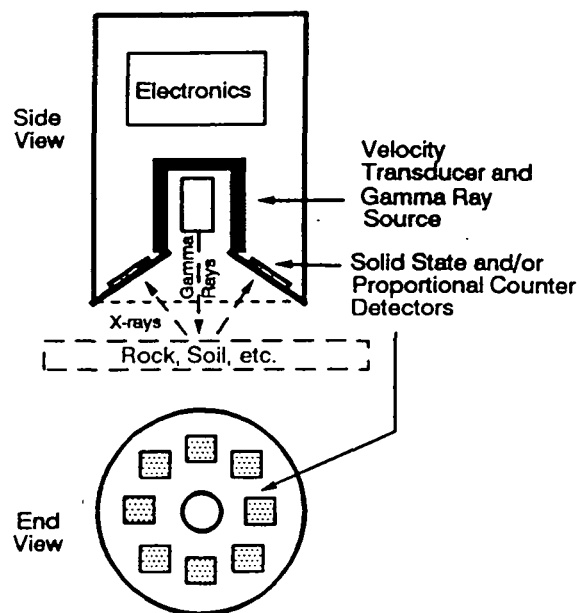


Fig. 1. BaMS schematic.

shielded from light, PIN detectors are suitable for detection of X-rays and gamma rays at energies required for Mössbauer spectroscopy (6.4 and 14.4 keV). Advantages of PIN detectors over proportional counters for planetary applications include small size (~0.2 cm³) and low operating voltage (<100 V).

We are currently assembling and testing a BaMS instrument (Fig. 1) employing a miniature loudspeaker drive and an array of PIN detectors to cover most of the 2 π backscatter surface area. Based on the mass and power consumption of brassboard components, we project a BaMS instrument that will meet target specifications for a flight unit of mass <500 g, volume <300 cm³, and power <2 W. During BaMS instrument development, analytical performance is evaluated with martian meteorite, martian analogue, and lunar samples.

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THE POTENTIAL UTILITY OF SPECTRAL REFLECTANCE AND EMISSION OBSERVATIONS TO MARTIAN LANDERS. Raymond E. Arvidson¹, Michael K. Shepard¹, and Benoit Rivard², ¹McDonnell Center for the Space Sciences, Department of Earth and Planetary Sciences, Washington University, St. Louis MO 63130, USA, ²Earth Observation Laboratory, Institute for Space and Terrestrial Science, York University, North York, Ontario, Canada M3J 3K1.

Estimates of surface thermal inertia derived from the Viking Infrared Thermal Mapper demonstrate that bedrock outcrops are rare [1]. Using IRTM data, Christensen [2] demonstrated that deviations in blackbody behavior over diurnal cycles could be modeled as a combination of high-thermal-inertia blocks and low-thermal-inertia, fine-grained sediments. The two Viking Lander sites are located in areas predicted to be among the blockiest on Mars. Viking Lander images demonstrate that the two sites exhibit blocks of a variety of sizes [3]. In addition, there is evidence for some bedrock outcrops at the Mutch Memorial Station [3]. Six-channel (0.4–1.0 μm) Viking Lander images show that most rocks have spectral reflectances comparable to terrestrial basalts that are thinly coated with palagonite or desert varnish [4]. Unfortunately, the six broadband channels undersampled the spectral properties of rock and sediments, making mineralogical identification tenuous at best.

The thesis of this abstract is to explore the additional mineralogical information that might have been obtained if the Viking Lander imaging system had the capability to acquire high-spectral-resolution reflectance and emission data. Would it have been possible to identify the mineralogy of bedrock, rock coatings, and sedimentary deposits that are ubiquitous at both landing sites? The answers may significantly affect measurement and planning strategies for future lander missions to Mars. Acquisition of spectral reflectance and emission data from a stationary or roving lander does not require sample preparation and can be obtained anywhere within the field of view of the imaging system. For roving landers, this ability would greatly increase the reconnaissance potential of the lander since compositionally interesting areas could be searched for before committing the rover to a direction of travel. Thus, high-spectral-resolution imaging data potentially offer a relatively inexpensive way to acquire large amounts of mineralogical information.

In this work, we address the problem of identifying bedrock mineralogy using high-spectral-resolution observations of blocks modified by wind and coated with fine-grained aeolian sediment and desert varnish. Samples of a number of natural rock surfaces, collected at the Lunar Crater Volcanic Field, Nevada, and in the Eastern Desert, Egypt [5], were used as analogues to blocks of the martian surface. Samples consisted of rhyolites, andesites, and basalts. Broken, fresh surfaces were also measured for control. Samples were measured with high-spectral-resolution reflectance (0.45–2.4 μm , ~15-nm resolution) and thermal emission (7–14 μm , ~50-nm resolution) laboratory instrumentation. Lighting and viewing geometries were selected to simulate the Viking Lander observations.

For these samples, the extension of reflectance data beyond the Lander's 1.0- μm limit provided information on the presence of olivine and pyroxene due to electronic transition features (at ~1 μm ; 1 and 2 μm respectively) and hydrous phases via the 2.1- to 2.4- μm vibrational features [5]. Further, spectra of coated and fresh surfaces tended to converge at longer wavelengths, suggesting a greater degree of transparency of the coatings as wavelength increases. At thermal emission wavelengths, the coatings were found to be less important. Bedrock mineralogy, including fundamental vibrations

associated with Si-O bonds, dominated the spectra. These preliminary experiments demonstrate that high-spectral-resolution reflectance and emission observations provide direct mineralogical information even in the presence of coatings. Further, the information is complementary in that absorption features due to charge transfers and electronic transitions show up in the visible and near-infrared, combination and overtone vibrational features also show up in the near-infrared, and fundamental vibrations dominate the infrared.

In summary, if the Viking Landers had been equipped with high-spectral-resolution reflectance and emission imaging capabilities, the mineralogy of bedrock, blocks, and rock coatings would have been discernible. Approaches for imaging instrumentation that acquire reflectance and emission data will be discussed at the workshop.

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DATABASE OF PROPOSED PAYLOADS AND INSTRUMENTS FOR SEI MISSIONS. N. G. Barlow, Syscom Development, Inc., Mail Code XI, NASA Johnson Space Center, Houston TX 77058, USA.

A database of all payloads and instruments proposed for lunar and Mars missions has been compiled by the author for the Exploration Programs Office at NASA's Johnson Space Center. The database is an outgrowth of the document produced by C. J. Budney et al. at the Jet Propulsion Laboratory in 1991 [1]. The present database consists not only of payloads proposed for human exploratory missions of the Moon and Mars, but also experiments selected or proposed for robotic precursor missions such as Lunar Scout, Mars Observer, and MESUR. The database consists of two parts: a written payload description and a matrix that provides a breakdown of payload components. Each payload description consists of the following information: (1) the rationale for why the instrument or payload package is being proposed for operation on the Moon or Mars; (2) a description of how the instrument works; (3) a breakdown of the payload, providing detailed information about the mass, volume, power requirements, and data rates for the constituent pieces of the experiment; (4) estimates of the power consumption and data rate; (5) how the data will be returned to Earth and distributed to the scientific community; (6) any constraints on the location or conditions under which the instrument can or cannot operate; (7) what type of crew interaction (if any) is needed; (8) how the payload is to be delivered to the lunar or martian surface (along with alternative delivery options); (9) how long the instrument or payload package will take to set up; (10) what type of maintenance needs are anticipated for the experiment; (11) stage of development for the instrument and environmental conditions under which the instrument has been tested; (12) any interface required by the instrument with the lander, a rover, an outpost, etc.; (13) information about how often the experiment will need to be resupplied with parts or consumables, if it is to be resupplied; (14) the name and affiliation of a contact person for the experiment; and (15) references where further information about the experiment can be found.

The payload matrix contains more specific information for each experiment than does the payload description. The payload matrix is an Excel chart containing information about the transport accommodations, deployed physical data, construction information, set-up

time and difficulty, surface accommodations, communication requirements, data formats, operation requirements, technology readiness level, and any unique requirements or comments for each payload. The detailed breakdown of the information in the payload matrix is as follows:

1. Transport Accommodations: mass, dimensions, volume, power, thermal control, human interaction, and robotic interaction.
2. Deployed Physical Data: mass, volume, dimensions, and location.
3. Construction: cleared surface area, excavation depth, and excavated volume.
4. Set-Up: set-up IVA time, set-up EVA time, robotic set-up time, assembly difficulty, and transport requirements.
5. Surface Accommodations: day power (operating and standby), night power (operating and standby), waste heat generated, heat rejection temperature, pressurized volume, and other services.
6. Communications: number of narrow data streams, number of wide data streams, number of voice data streams, and number of video channels.
7. Data: output data format, frequency, maximum data rate, data volume, optimal storage method, optimal transmittal method, and *in situ* data processing requirements.
8. Operations: number of robotic hours/week, number of IVA hours/week, number of EVA hours/week, training level, and crew specialist requirements (type and time needed).
9. Technology Readiness: level.
10. Unique Requirements and Comments.

The payload description and matrix are designed to provide scientists and engineers involved in the Space Exploration Initiative programs with a continuously updated database of the various experiments that have been proposed for robotic and human missions. The database contains information on all instruments proposed, not just those that have been officially selected for a particular mission.

The database is continually evolving as new instrumentation is proposed for the various missions to the Moon and Mars. Any additions, comments, or suggestions about the database should be directed to the author at the above address.

References: [1] Budney C. J. et al., eds. (1991) *SEI Science Payloads: Descriptions and Delivery Requirements*, JPL D-7955.

AN OVERVIEW OF IMPORTANT SCIENTIFIC QUESTIONS ABOUT ATMOSPHERE-SURFACE INTERACTIONS ON MARS. Bruce Fegley Jr., Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis MO 63130-4899, USA.

Introduction: The past three decades of Mars exploration and observation have led to a dramatic increase in our knowledge of the Red Planet, and have shown the seminal roles played by atmosphere-surface interactions such as condensation and sublimation of CO₂, the dominant atmospheric constituent, and the condensation and evaporation of water vapor, an important minor constituent. Other types of atmosphere-surface interactions are also believed to be important under martian surface conditions, but have not been firmly identified. In this presentation I review some of the key issues about atmospheric composition, lithospheric composition, and atmosphere-surface interactions (e.g., chemical weathering) that remain unresolved, and mention possible measurements that may be used to address these questions. This sets the stage for many of the presentations to be given at this workshop.

Atmospheric Composition: The key questions about martian atmospheric composition include several related to the detection, concentration, transport, and variations of various atmospheric species that are either known to interact with the martian surface or are thought to do so. Thus, questions such as the following need to be addressed: (1) The spatial and temporal variation of water vapor in the troposphere. Long-term, *in situ* data are needed to complement and extend the results of Earth-based observations and the Viking MAWD experiment. (2) The spatial and temporal variation of ozone, a known product of martian atmospheric photochemistry. (3) The behavior of CO₂, H₂O, O₃, and other predicted reactive trace gases that are products of atmospheric photochemistry in the planetary boundary layer. We observe that the martian surface is both a source and a sink of CO₂ and water vapor. It is reasonable to surmise that the surface of Mars, like the surface of the Earth, is both an emitter and a receiver of different atmospheric trace gases. Of course, this is for different reasons than on the Earth, e.g., the presence of energetic solar UV radiation and the lack of biological activity on Mars. To a first approximation, qualitatively different behavior in the planetary boundary layer is expected over the polar caps and over the rest of the rocky surface. (4) The detection and monitoring of as-yet unobserved, but predicted, products of atmospheric photochemistry. These products include H₂, H₂O₂, NO, NO₂ and several highly reactive radicals and atoms HO₂, OH, O, and H [1-4]. Hydrogen peroxide and other more complex peroxides that may form from it have attracted great interest as possible explanations for the activity observed by the Viking life detection experiments. Peroxides may also be important oxidants in martian soils and "precipitation" [5]. Oxidation reactions of H₂O₂ with Fe-bearing minerals and other transition-metal-bearing minerals are energetically very favorable and may play a role in chemical weathering on Mars. (5) The measurement and long-term monitoring at the martian surface of CO, O₂, O₃, and other products of photochemistry in the CO₂-H₂O system is also potentially important for determining the importance of heterogeneously catalyzed reactions in maintaining the stability of the martian atmosphere against photochemical destruction. The current gas-phase photochemical models need to invoke either unreasonably high K_{eddy} coefficients or unreasonably high water-vapor concentrations in order to account for the photochemical stability of the atmosphere [1-4,6]. The importance of these heterogeneously catalyzed reactions is not well constrained at present, but may be significant.

The isotopic composition of the different atmospheric gases is also an important issue for several reasons: (1) The D/H ratio and oxygen isotopic composition of water vapor, and the carbon and oxygen isotopic composition of CO₂ are important for assessing models of volatile cycling between the atmosphere, regolith, and polar caps. (2) High-accuracy and high-precision data comparable to those from laboratory measurements of SNC meteorites are also desirable for comparison with these putative martian samples. (3) A knowledge of isotopic fractionations between different atmospheric gases (e.g., oxygen isotopes in water vapor, CO₂, CO, O₂, O₃, etc.) would help constrain models of atmospheric chemistry and would be important for comparisons to terrestrial atmospheric chemistry.

Surface Composition and Chemical Weathering: Key questions about the composition of the surface of Mars include the following: (1) Determination of the chemical, isotopic, and major-element mineralogical composition of bulk rocky material at several sites on the surface. This is important for comparison with the Viking XRF data, for comparison with analyses of SNC meteorites, and for constraints on cosmochemical modeling of the composition of Mars. Important isotopic data include the ¹⁷O/¹⁶O and ¹⁸O/¹⁶O ratios at an

accuracy and precision sufficient to resolve the expected small difference from the terrestrial mixing line, and data for several isotopic systems such as Nd-Sm, Rb-Sr, U-Pb, Pb-Pb, Hf-Lu, etc., used for geochronology. (2) Determination of the nature, abundance, and geographical variations of Fe-bearing minerals on the martian surface. Various Mössbauer spectroscopy instruments for doing this will be discussed at the workshop. (3) Determination of the nature and abundance of minor and trace phases commonly expected to be present on the martian surface. Such phases include carbonates, nitrates, sulfates, and hydrated minerals [7]. Many of these phases are expected to be products of chemical weathering reactions [8].

Several of the issues related to determining the nature and extent of chemical weathering at the present and during the past include the following: (4) Measurements of the chemical, isotopic, and mineralogical composition of weathering products found on different rocks and minerals and similar measurements on the underlying material. When coupled with measurements of the thickness of the chemically weathered layer, the age of the layer (e.g., from cosmogenic nuclides), and the atmospheric composition, this would give a knowledge of the gaseous and solid reactant compositions and of the solid reaction product. Information about the timescale of the weathering process would also be obtained. (5) Measurements of the geographic variations (if any) in the nature and abundance of weathering products. (6) Measurements of the relationship (if any) between the nature and abundance of chemical weathering products on minerals and rocks and solar UV illumination at the same site. The importance of photochemical weathering on Mars is a controversial topic that is being actively investigated by different laboratory experiments. *In situ* measurements that can deconvolve present-day and "fossil" weathering products will go a long way toward answering questions about the importance of photochemical weathering on Mars.

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A POSSIBLE USE OF SEMICONDUCTOR GAS SENSOR INSTRUMENT FOR INVESTIGATION OF UV-DECOMPOSITION OF MARTIAN SALTS AND RELEASE OF Cl- AND S-CONTAINING GASES TO THE ATMOSPHERE. M. V. Gerasimov, Space Research Institute, Russian Academy of Sciences, ul. Profsoyuznaya, 84/32, Moscow, Russia.

Martian soil contains a rather high concentration of salts composed mainly of sulfates and chlorides. Concentration of sulfates in martian soil is estimated to be about 8–15% and concentration of chlorides 0.5–1.5% [1]. The composition of martian salts is uncertain, but probably is a mixture of Mg, Ca, and Fe sulfates and chlorides of Mg, Ca, Na, and Fe. The action of solar UV illumination on the surface of the martian soil can result in the destruction of salts and release of S- and Cl-containing gases (mainly SO₂ and Cl₂) to the atmosphere. Trapping of these gases by atmospheric aerosols or dust

forms a certain step in cycles of S and Cl on Mars. Currently we do not have much information about the mobility of S and Cl on Mars. The concentration of SO₂ and Cl₂ in the martian atmosphere is considered to be low (<0.1 ppm) [2,3] and cannot be measured by orbiter spectroscopy methods down to the martian surface. For this reason the *in situ* measurement of concentrations of S- and Cl-containing gases in the martian near-surface atmosphere can provide important information about the role of UV radiation in S and Cl cycles.

An experiment by Obvintseva et al. [4] measured the destruction of AgCl salt under the action of UV radiation (1–300 nm). With absorption of 10¹²–10¹³ photons s⁻¹ the flow was 5×10¹¹ to 5×10¹² cm⁻² s⁻¹ of Cl atoms from the surface of AgCl salt. Decomposition of AgCl salt proceeded with release of Cl₂ molecules and Cl atoms. The flow of Cl gases was measured using semiconductor gas sensors on the basis of ZnO and NiO oxides. This experiment has two important outcomes: (1) decomposition of salts under the action of UV luminosity can be a real and noticeable process for the martian environment and (2) semiconductor gas sensors can be valid for measurement of gases that evolve during UV decomposition of salts. A semiconductor gas sensor analyzer is now in preparation for the Mars rover within the Russian Mars '94, '96 missions. It is a portable instrument weighing less than 200 g. The main purpose of this instrument is to measure minor components of the martian atmosphere such as H₂O, CO, O₂, and H₂. The possible measurement of S- and Cl-containing gases using a semiconductor gas sensor analyzer is discussed.

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N 94 - 22433

DETERMINATION OF MARTIAN SOIL MINERALOGY AND WATER CONTENT USING THE THERMAL ANALYZER FOR PLANETARY SOILS (TAPS). James L. Gooding¹, Douglas W. Ming¹, Judith H. Allton², Terry B. Byers², Robert P. Dunn², Frank L. Gibbons², Daniel B. Pate², and Thomas M. Polette², ¹Code SN, NASA Johnson Space Center, Houston TX 77058 USA, ²Lockheed Engineering and Sciences Company, 2400 NASA Road 1, Houston TX 77058, USA.

Physical and chemical interactions between the surface and atmosphere of Mars can be expected to embody a strong cause-and-effect relationship with the minerals comprising the martian regolith. Many of the minerals in soils and sediments are probably products of chemical weathering (involving surface/atmosphere or surface/hydrosphere reactions) that could be expected to subsequently influence the sorption of atmospheric gases and water vapor. Therefore, identification of the minerals in martian surface soils and sediments is essential for understanding both past and present interactions between the Mars surface and atmosphere. Clearly, the most definitive mineral analyses would be achieved with well-preserved samples returned to Earth-based laboratories [1]. In advance of a Mars sample return mission, however, significant progress could be made with *in situ* experiments that fill current voids in knowledge about the presence or abundance of key soil minerals such as clays (layered-structured silicates), zeolites, and various salts, including carbonates. TAPS is intended to answer that challenge by providing first-order identification of soil and sediment minerals.

TAPS combines a differential scanning calorimeter (DSC) with an evolved-gas analyzer (EGA) based on single-function gas sensors

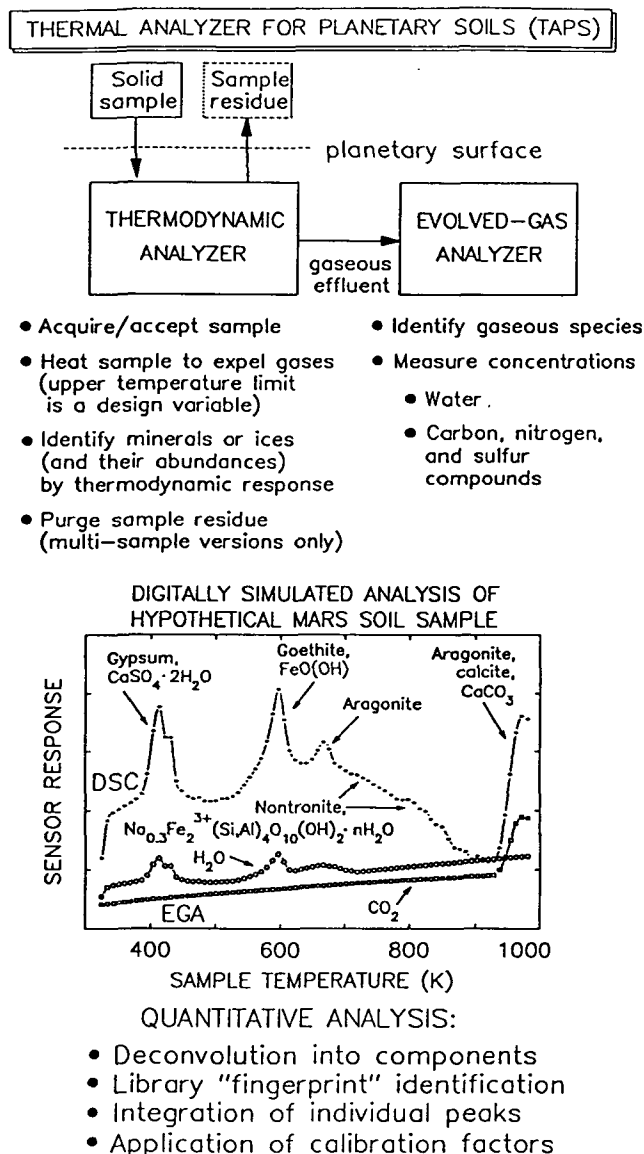


Fig. 1. Functions and simulated data for a TAPS experiment appropriate for small Mars landers. Correlation of DSC peaks with H_2O or CO_2 peaks from EGA single-function gas sensors permits positive recognition of hydrate or carbonate minerals respectively.

located in the DSC effluent gas stream (Fig. 1) [2]. DSC is the quantitative measurement of the enthalpic response of a material to a systematic change in temperature; the fundamental properties measured are enthalpies and temperatures of phase transitions and constant-pressure heat capacities [3]. DSC superficially resembles differential thermal analysis (DTA), but is more quantitative and versatile [3]. High-quality DSC analyses can be obtained on only a few milligrams of solid materials.

A DSC/EGA combination applied to Mars can identify minerals according to their heat-flow "fingerprints," using pattern-recognition strategies that are generally similar to those employed in spectrophotometry [2,4]. The principal strength of DSC in the planetary context is identification of ices and volatile-bearing minerals, including clays, hydrous salts and oxides, and carbonates. Given the mineral identities, characteristic enthalpic peaks can be

integrated to yield relative proportions of the minerals present. DSC detection limits for hydrous minerals range from about 10 wt% for clays to <1 wt% for iron oxyhydroxides and salts [5]. Unlike spectrophotometry, DSC results are relatively insensitive to particle coatings or other matrix effects. Although the appearance of a given heat-flow curve can depend on the physical characteristics of the sample, integrated ratios of enthalpic peaks change less severely with physical properties than do peaks in reflectance spectra.

Although the EGA function is often equated with a gas chromatograph or mass spectrometer, smaller and simpler gas sensors offer compact yet powerful alternatives. For example, capacitive-polymer humidity sensors represent a recent technology [6] that our work has shown can achieve precise EGA measurement of water with minimal complexity [7]. Similar progress on microchemical sensors specific to other gases is expected to provide additional opportunities for a comprehensive EGA without the slow throughput of gas chromatographs or the vacuum requirements of mass spectrometers.

DSC-based experiments have been previously designed but never flown on spacecraft. The Planetary Soil Water Analyzer (PSWA) experiment [8], which included a DSC backed by an electrolytic-cell detector for evolved water vapor, was developed in the early 1980s as a post-Viking follow-on experiment for Mars. However, no further Mars landing missions were flown and the PSWA project was discontinued. A preliminary design for a DSC experiment, backed by a gas chromatograph as EGA, was included during the middle 1980s in plans for the Comet Rendezvous and Asteroid Flyby (CRAF) Penetrator-Lander, but the instrument was never built and CRAF was cancelled.

In 1989, concepts for DSC-based planetary experiments were renewed as the TAPS project with emphasis on applications to small Mars landers. Work to date has addressed packaging concepts, integrated sample-acquisition mechanisms, determination of sensitivity requirements, and evaluation of candidate water sensors. Using 1980s technology, a version of TAPS packaged for Mars applications is estimated to have the following attributes: 1.2 kg mass, 850 cm³ volume, 5 W peak power, and 1.5 Whr per analysis. Design, fabrication, and demonstration tests are in progress for a prototype that will be complete in 1993.

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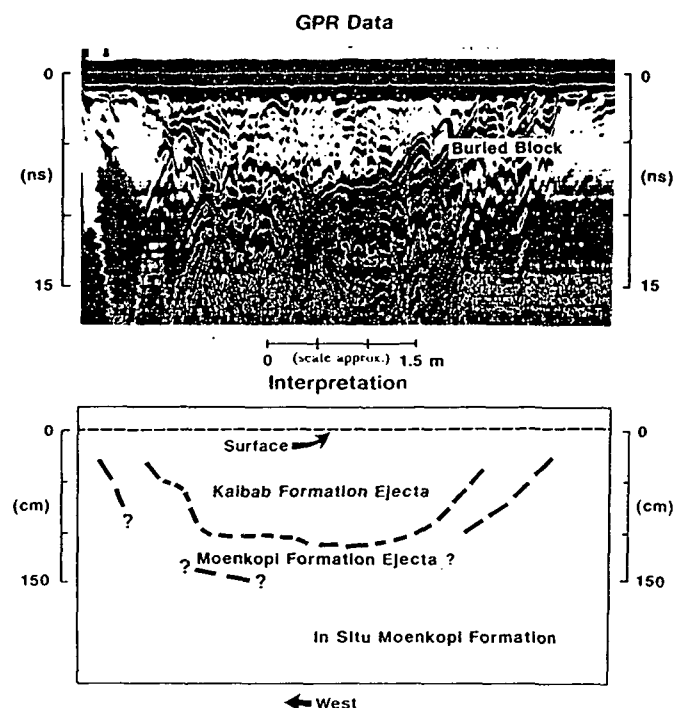
GROUND-PENETRATING RADAR AS A TOOL FOR INVESTIGATING NEAR-SURFACE STRATIGRAPHY ON MARS. J. A. Grant and P. H. Schultz, Department of Geological Sciences, Brown University, Providence RI 02912, USA.

Despite the highly successful outcome of previous planetary missions to Mars, fundamental questions remain regarding the interaction between atmospheric and surface processes. For example, many characteristics of the near-surface stratigraphy (depths less than ~30-40 m) and soils on the planet remain largely unknown. Additionally, the nature and origin of fine-grained deposits mantling portions of the cratered uplands and the near-surface of the northern

lowlands (e.g., [1–4]) preserve the long-term sedimentary history of surface-atmosphere exchanges through time, but remain unexplored. Ground-penetrating radar (GPR) is a proven and standard instrument capable of imaging the subsurface to several tens of meters and could help resolve these issues through definition of the geologic record during future Mars missions. GPR data would also provide context for interpreting results of other surface analyses (e.g., elemental or mineralogical).

Previous terrestrial experience (e.g., [5,6]) with a GPR and associated transducer frequencies between 50 and 500 MHz demonstrates the effectiveness of the instrument in definition of stratigraphy up to 30–40 m depth [5] and a resolution of up to 10–20 cm [6]. Moreover, successful GPR deployment in and around Meteor Crater, Arizona, Odessa Craters, Texas, and the Rio Cuarto Craters, Argentina, highlights the capabilities of GPR in planetary settings [6]. Data collected along short transects (10–100 m) around these craters using an analogue GPR produced easily recognized stratigraphic markers corresponding to different ejecta compositions, alluvium, calcic soils, and *in situ* bedrock (Figs. 1 and 2) all with dielectric constants of 4–10. Excavation of groundtruth pits demonstrates that the GPR reflectors are within 5–10 cm of the actual position of geologic contacts. Prominent stratigraphic reflectors were identified even where calcic soils were well developed (Fig. 2). Coupled with their compact size, these characteristics imply GPR could define shallow martian stratigraphy and should be considered as an instrument on future rover missions.

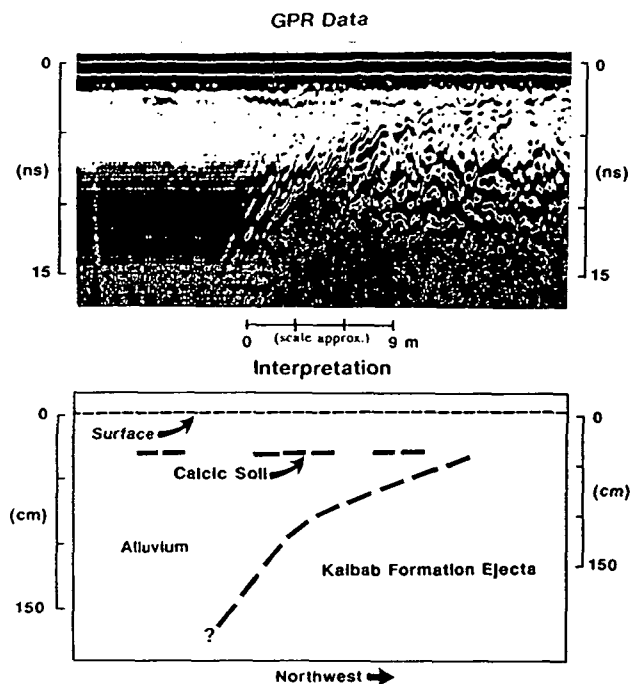
Meteor Crater Distal Ejecta Lobe Transect



Data collected using Geophysical Survey System, Inc. SIR-3 and 500 MHz Transducer

Fig. 1. Analogue GPR transect across distal ejecta lobe superposing low butte 1.1 km north-northwest of Meteor Crater. Radar pulse travel time is in nanoseconds and the depth is in centimeters. Ejecta derived from two excavated lithologies is identifiable as is the underlying bedrock. Contacts were confirmed by excavation.

Meteor Crater Medial Drainage Transect



Data collected using Geophysical Survey Systems, Inc. SIR-3 and 500 MHz Transducer

Fig. 2. Analogue GPR transect through blocked drainage ~0.5 km south of Meteor Crater. Radar pulse travel time is in nanoseconds and the depth is in centimeters. Ejecta and alluvium are clearly distinguished. The top of the calcic soil horizon (Bk horizon) is also identifiable. Discontinuous reflectors in the ejecta are caused by buried blocks. Contacts were confirmed by excavation.

Definition of shallow stratigraphy on Mars using rover-mounted GPR might resolve several issues regarding surface and atmospheric evolution when accompanied by groundtruth from penetrators or cores. First, the Viking landers revealed high sulphur contents in surface duricrusts [7] whose origin may be related to either precipitation during groundwater evaporation [7] or deposition of volcanic aerosols [8]. GPR could define the occurrence of these sediments: Locally varying deposits would support a groundwater source while uniform, discretely layered accumulations imply fallout of aerosols. Second, models for atmospheric evolution suggest considerable carbonates should have formed in the regolith [9]; however, minimal concentrations are observed telescopically [10]. Identification of calcic soils at Meteor Crater implies similar horizons would be detected on Mars if near the surface. Third, occurrence of near-surface brines has been proposed and subsequently questioned [11,12] and models for the latitudinal distribution of ground ice/water (e.g., [13]) are in wide use. GPR mapping of lateral and depth variations in dielectric constant could test such models. Finally, GPR transects could help identify optimal coring locations and might reveal buried volcanic flows, superposed ejecta deposits, paleosols, or regolith depth. In the absence of groundtruth, GPR should define shallow stratigraphic complexity, thereby providing a context for interpreting data from other instruments.

Mars landing and GPR deployment proximal to thick unconformable deposits or within the northern lowlands would allow additional questions to be addressed. Unconformable deposits can accumulate by volcanic and eolian processes and may relate to accumulation

during intervals of polar wandering or more equable climate [1]. GPR transects would identify layering in the deposits and any lateral variations in thickness. Accumulation during element or polar climate epochs should be sensitive to orbital forcing, thereby resulting in continuously layered stacked sequences. By contrast, volcanic processes [2] might produce less continuous, variably thick layers separated by interruption paleosoils.

Formation of the northern lowland surface has been attributed to alluvial, volcanic, eolian [3], and, more recently, pelagic deposition [4]. Each process produces characteristic stratigraphy that should be distinguishable with the GPR. For example, debris flows would form poorly sorted and crudely layered deposits, whereas other fluvial deposits may be better sorted, more uniformly bedded bar and swale features. Stratigraphy in both types of alluvium would be limited in lateral extent. Conversely, pelagic deposition would form well-sorted, fine-grained continuous deposits devoid of bedforms and possibly interbedded with turbidites. Volcanic and eolian beds can be similarly characterized. Based on the ease in identifying differing depositional units with GPR in terrestrial settings (Figs. 1 and 2), such formations might also be distinguished on Mars.

GPR data collected around terrestrial impact craters discriminates *in situ* bedrock, ejecta, alluvium, and calcic soils, thereby highlighting the potential of the instrument in a variety of planetary settings. Inclusion of a GPR on a Mars rover would define shallow stratigraphy and could map changing dielectric constants in the substrate if accompanied by groundtruth. In turn, this information could be used to identify compositional units and help constrain interactions between surface and atmospheric processes.

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ANALOGUE OF HAND-HELD LENS AND OPTICAL MICROSCOPE FOR MARTIAN *IN SITU* STUDIES. Petr Jakes, Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston TX 77058, USA.

The simple hand-held lens (magnification 10×) has been one of the most powerful tools for the examination of rocks and minerals over past centuries. In the terrestrial environment the determination of mineral phases by optical devices (microscopes), combined with the observation of textural relationships of phases and bulk mineral composition, usually precedes the use of sophisticated techniques such as electron microscopy, isotope analysis, etc.

The suggested instrument is a modified optical microscope that uses a CCD digital camera equipped with microscope optics and LED illumination. The microscope-camera is capable of providing an optical "visible light image" of the surface in an area of approximately 4 cm² with high resolution (at maximum magnification and hence smaller area) in the range of 0.005 mm. Deep-focus image array uses the potential of computer image processing to produce pseudo-SEM images.

The instrument complements remote sensing and spectral data in determining the phase composition of particles and their morphological features. The microscope is complemented by an analyzing instrument that combines the optical tool with the source of X-ray radiation and an X-ray-sensitive detector in order to perform *in situ* semiquantitative chemical analysis of particles in the view of the microscope.

The idea of a deep-focus imaging instrument uses movable focus optics (either continuous and/or step by step) to provide a series of images of the same object with different focus levels. The images of the same object are computer processed to obtain a deep-focus view (pseudo-SEM image) of surface particles, thus extending the identification capabilities of the instrument. The computer processing uses techniques available for image processing of, e.g., aerial photography.

The power of observation of the human eye, which may seem at present too unsophisticated, should not be omitted in any future martian mission and should not be unjustly replaced by highly sophisticated techniques. The planetary processes, either endogenous or exogenous, are recorded in both chemical composition and rock textures. Soils and regoliths record the history of exchange of energy/material between the planet's surface, atmosphere (hydrosphere), and surrounding space in the shapes and arrangement of surface particles. The available data on the martian surface come from several independent observations: (1) remote sensing techniques such as infrared and near-infrared spectra, (2) analytical XRF data from two Viking landing sites, (3) visual analysis of surface features on a scale from a few centimeters up to features thousands of kilometers in size, and (4) the established common wisdom that SNC meteorites were derived from the martian surface. Though it seems that data are plentiful, the speculations on processes involved in the formation of the martian surface are still little constrained (see abstracts in *Workshop on Chemical Weathering on Mars*, LPI Technical Report 92-04, Part 1). If an instrument providing close-up views of the surface with submillimeter-scale resolution had been available on the Viking lander missions, the present-day models of the phase composition of the martian surface would be much less speculative.

The early attempts to obtain close-up "visible light" images of planetary surfaces with fine (centimeter- to millimeter-sized) resolution were not always considered successful by the scientific community. Apollo 11 stereophotography, Viking-Mariner close-ups of Mars' surface, and close-up images of Venus' surface by Venera 13 and 14 were not as impressive as "aerial" images of large areas of the planets. Therefore, some reservations on the employment of "microscope techniques" exist. The resolution in the early images was (except for Apollo 11) at best around 1 cm and the presence of other data (e.g., chemical analyses) has overshadowed the value of images. The use of wavelengths other than visible light with even worse resolution (e.g., reflectance spectra, IR spectroscopy) were multiply interpreted.

Optical imagery will contribute to phase identification and characterization of particle shape. The close-up look at the martian surface, however, is fully justified. It will complement the knowledge of chemical compositions of the martian surface and will allow more precise interpretation of exogenous processes.

DEVELOPMENT OF A MÖSSBAUER BACKSCATTERING SPECTROMETER, INCLUDING X-RAY FLUORESCENCE SPECTROSCOPY, FOR THE *IN SITU* MINERALOGICAL ANALYSIS OF THE MARS SURFACE. G. Klingelhöfer, J. Foh, P. Held, H. Jäger, R. Teucher, and E. Kankleit, Inst. f. Kernphysik, TH Darmstadt, Schlossgartenstrasse 9, D-6100 Darmstadt, Germany.

The element iron is abundant on the surface of Mars (~13% by weight), as was determined by X-ray fluorescence analysis during the Viking mission in 1976. But the type of Fe oxides and silicate minerals is not known. Therefore, for the *in situ* mineralogical analysis of the Mars surface (soil as well as rocks), ^{57}Fe Mössbauer spectroscopy is an obvious choice [1].

Mössbauer spectroscopy is a nuclear technique, measuring the electric and magnetic hyperfine interaction of the nucleus with its atomic surrounding. The hyperfine interaction leads to an energy shift of the nuclear states and/or a splitting caused by magnetic or electric fields. It depends strongly on crystal structure, chemical bonding, temperature, crystallite size, etc. Thus, by Mössbauer spectroscopy (MS) the mineralogical composition, its physical and chemical properties, especially the charge state of the Mössbauer isotope, the size of small particles, and the magnetic properties of the sample can be determined, which is of fundamental interest in the investigation of the martian surface.

The hyperfine splitting is measured by resonance scattering (or absorption) of low-energy γ -quanta in the sample. The magnitude of resonant scattering of these γ -quanta (14.4 keV in the case of ^{57}Fe) is measured as a function of a defined energy shift (\rightarrow Mössbauer spectrum), produced by the Doppler effect, e.g., a defined velocity of the γ source.

Using a backscattering geometry, the soil and the rocks can be studied as found; no sample preparation is necessary. A preliminary construction scheme of our spectrometer is given in Fig. 1 and in [2], which is similar to a system proposed by a U.S. team [7].

The main parts are the electromechanical vibrator [3,5] mounted in the center of the instrument, the detector system consisting of silicon-PIN-diodes, the electronics for the drive and the detectors, and the ^{57}Co Mössbauer source. The control and data handling is done by a transputer (microprocessor) [4]. The total weight of the system is less than 400 g, with a maximum power consumption <1.5 W. The total volume will be below 700 cm³ (comparable to a Coca-Cola can).

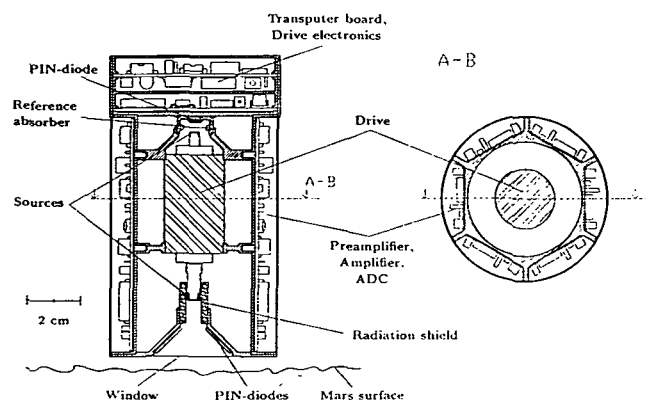


Fig. 1. Mössbauer backscattering spectrometer.

The instrument allows the recording of Mössbauer spectra using the backscattered 14.4-keV γ -quanta, and the 6.4-keV Fe X-rays, emitted after internal conversion of the 14.4-keV Mössbauer state. Because of the different escape depth of these two types of photons we expect some (limited) depth resolution. Because of low intensity of the Mössbauer signal the shielding between source and detector should be sufficient to optimize the signal-to-noise ratio. The elastic and inelastic nonresonant scattering of the 14.4-keV quanta in the sample may significantly affect the signal-to-noise ratio. Because of its angle dependence the geometry of the detector arrangement has to be considered very carefully. The surface roughness (or the albedo of the surface in the 14.4-keV region) also has an influence on the signal-to-noise ratio.

For interpretation of the Mössbauer spectra it is of interest to measure the spectra as a function of temperature, and also to determine the elemental composition of this sample (soil, rock). Different Fe compounds show different temperature dependences of HFI. Because an active cooling of the sample does not seem possible, we want to measure MS spectra as a function of the martian surface temperature, which varies between about +20°C and -80°C (day and night, depending on the landing site).

By measuring the X-ray fluorescence (XRF) radiation, excited in the sample mainly by the 6.4-keV X-rays, 14.4-keV, and 122-keV γ rays emitted from the ^{57}Co Mössbauer source, the chemical composition of the sample could be determined. For example, the shape of the Mössbauer spectrum of $\alpha\text{-(Fe}_{1-x}\text{Ti}_x)_2\text{O}_3$ depends strongly on the Ti content and also on the crystallite size [1]. Small magnetic crystallites are often found to be superparamagnetic. Knowing the Ti content in the sample, the influence of these two effects could be distinguished.

For XRF the energy resolution of the PIN diodes, used for Mössbauer spectroscopy, has to be improved or another type of photon detector has to be used, for example, HgI_2 [8,9].

Another interesting point is the investigation of the martian surface as a function of depth. This could be done by using the 14.4- and the 6.4-keV radiation (see above), and also, in the case of the Mars '96 mission, by using the possibility of digging with the wheels of the rover, which will be placed on the surface of Mars [1,2].

Using a prototype of the setup shown in Fig. 1, but with only one diode, we have recorded MS spectra at 14.4 keV for a sample containing about the same amount of iron as found on the Mars surface by Viking (Mars sample analogue). From these measurements we conclude that spectra with sufficient statistical quality can be recorded within about a few hours using a fully equipped spectrometer.

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MAGNETIC PHASES ON THE MARTIAN SURFACE. J. M. Knudsen¹ and L. Vistisen², ¹Physics Laboratory, H. C. Ørsted Institute, Universitetsparken 5, DK-2100, Copenhagen Ø, Denmark, ²Niels Bohr Institute, Blegdamsvej 17, DK-2100, Copenhagen Ø, Denmark.

The Viking landers on Mars were equipped to detect magnetic particles, and a remarkable finding was that the martian soil adhered nearly equally well to both strong and weak magnets on board the landers [1]. It was concluded that every particle making up the dust contained 1–7% of a strongly magnetic mineral. The nature of the magnetic mineral in the martian soil is not known with certainty.

The SNC meteorites, believed to come from Mars, contain a ferrimagnetic phase (titanomagnetite). Magnetic fractions of the meteorites Nakhla and Zagami have been studied by Mössbauer spectroscopy. The magnetic properties of the two meteorites, i.e., saturation magnetization, Néel point, etc., are very different, but both Zagami and Nakhla contain titanomagnetite. If SNC meteorites are indeed martian surface rocks, it seems reasonable to conclude that the surface basalts of Mars contain a magnetic phase. This is assumed in the following.

As both the soil and the rocks contain magnetic phases, it is evident that instrumentation for the study of magnetism on Mars is significant.

Soil: There are several possibilities for the origin of the magnetic phase in the soil. Let us mention two (certainly not the only ones). (1) The magnetic phase could have formed as a weathering product, inherited directly from the underlying basaltic base rock. In that case the phase would probably contain titanium [2]. (2) The magnetic phase could have formed via precipitation of Fe(III) compounds in liquid water. In that case the phase will probably be rather pure $\gamma\text{-Fe}_2\text{O}_3$ or Fe_3O_4 .

The various chemical pathways thus lead to a somewhat different structure and composition of the magnetic phase, and we may learn about the evolution of the surface of Mars through the identification

of the phase. The identification of the magnetic mineral would be a simple matter in the laboratory, difficult but perhaps possible through robotic experimentation on Mars.

By means of Mössbauer spectroscopy it will be possible to distinguish between maghemite and magnetite [3,4]. It may, however, be problematic from a Mössbauer spectrum alone to decide if the phase in question contains titanium as impurity. This may possibly be done by means of a simple piece of instrumentation described below.

Instrument for Measurement of Magnetic Properties: During the Viking mission, magnets to study both the surface soil and airborne dust were successfully applied. A simple extension of the Viking experiment would involve a disc with a number of magnets that would produce different magnetic fields and field gradients at the disc surface. With an array of, say, eight magnets it should be possible to determine a saturation magnetization within a factor of 2. Furthermore, if the dust at the disc of magnets could be heated, for instance by means of a simple parabolic mirror reflecting (and concentrating) the sunlight on the dust adhering to the magnet, it would be possible to determine (approximately) at which temperature the dust falls off the magnets. If this is accomplished, and a Mössbauer spectrum of the dust is available, the magnetic phase in the martian fines has been identified.

Figure 1 illustrates the application of Mössbauer spectroscopy to the study of a terrestrial red tropical soil from Brazil [5]. The letter V is for classification. The spectrum marked V1m is the Mössbauer spectrum of a sample prepared from V1 by magnetic separation.

This Brazilian soil has about the same magnetic properties as the martian soil. The phase responsible for the magnetism of the Brazilian soil is titanomaghemite, with the approximate composition $(\text{Fe}_{0.75}\text{Ti}_{0.25})[\text{Fe}_{1.25}\text{Ti}_{0.25}\square_{0.5}]\text{O}_4$, () tetrahedral sites, \square vacancies. A magnetic separation will not be possible on Mars, but even without separation the magnetic phase may, from the Mössbauer spectrum on Fig. 1, be clearly identified as maghemite. It is, however, not possible to infer the titanium content. Pure maghemite transforms to hematite at 320°C. By measuring the approximate value of the saturation magnetization by means of the disc of magnets, and by measuring the temperature at which the dust falls off the magnets, it may be possible to give a rough estimate of the titanium content of the sample.

Complications: If it is decided to include the suggested disc (and heating procedure) in the payload of a spacecraft to Mars, many simulation experiments have to be done. The magnetic properties of titanomaghemite—and maghemite with other isomorphous substitutions (Al, Mn, etc.)—are complicated, and the stability of maghemite containing impurities has to be investigated extensively.

Magnetic Phase in the Base Rocks on Mars: The fact that SNC meteorites contain a ferrimagnetic phase promises a rich field of paleomagnetic investigations on Mars if the planet ever generated a global field. New instrumentation for this activity has been described elsewhere [6].

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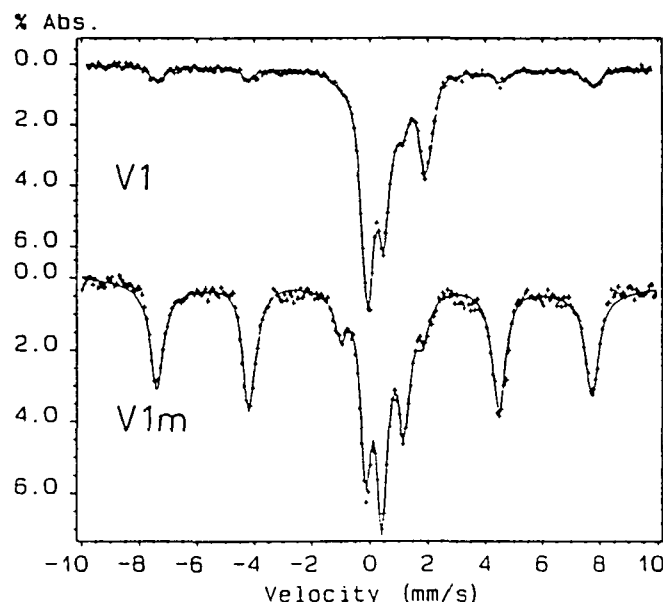


Fig. 1. Transmission Mössbauer spectra at room temperature for a sample from Brazil. From [5].

MASS SPECTROMETRIC STUDIES OF THE INTERACTION OF MARTIAN ATMOSPHERE GAS COMPONENTS WITH FERRIC OXIDE SURFACE UNDER UV ILLUMINATION. A. P. Koscheev¹ and L. M. Mukhin², ¹Karpov Institute of Physical Chemistry, Moscow, Russia, ²Space Research Institute, IKI, Moscow, Russia.

Photostimulated interaction of gases with metal oxides could be interesting for the problem of photochemical weathering on Mars. The martian rocks contain some photoactive oxides such as Fe_2O_3 , TiO_2 , etc., and there is enough UV radiation at the martian surface to stimulate the gas-surface reactions.

We have used mass spectrometry and thermodesorption spectroscopy methods to study some aspects of interaction of H_2O , CO_2 , CO , and O_2 and their mixture with the surface of Fe_2O_3 powder in the dark conditions and under UV illumination at temperatures 200–300 K and pressures 10^{-1} – 10^{-4} Torr.

In the dark conditions the chemisorption of CO_2 and H_2O was observed and these molecules can be removed from the surface of Fe_2O_3 only by heating or by UV irradiation. We have observed the blocking effect of preadsorbed H_2O molecules on adsorption of CO_2 . The adsorbed H_2O molecules also caused the appearance of a new, tightly bound state of adsorbed CO_2 and the filling of this new state may be increased by UV illumination.

The adsorbed CO molecules do not desorb as CO from the Fe_2O_3 surface. The only product of thermo- and photodesorption observed in this case was CO_2 and the efficiency of CO_2 photostimulated formation from CO on Fe_2O_3 surface was increased with surface oxygen concentration. Some aspects of catalytic oxidation of CO on the Fe_2O_3 surface under illumination were studied.

The experimental results are discussed in terms of CO_2 - H_2O , CO - O_{lat} , and CO - O_{ads} surface complex formation and in terms of their behavior under UV illumination.

DOES UV INSTRUMENTATION EFFECTIVELY MEASURE OZONE ABUNDANCE? Bernhard Lee Lindner, AER, 840 Memorial Drive, Cambridge MA 02139, USA.

Measurements of O_3 on Mars provide significant information about the chemistry and composition of the atmosphere [1], including long-term changes [2]. The most extensive and accurate data were inferred from the Mariner 9 UV spectrometer experiment, some of which are reproduced in Fig. 1. Mars O_3 shows strong seasonal and latitudinal variation, with column abundances ranging from 0.2 $\mu\text{m-atm}$ at equatorial latitudes to 60 $\mu\text{m-atm}$ over the northern winter polar latitudes [1] (1 $\mu\text{m-atm}$ is a column abundance of 2.689×10^{15} molecules cm^{-2}).

The Mariner 9 UV spectrometer scanned from 2100 to 3500 Å in one of its two spectral channels every 3 s with a spectral resolution of 15 Å and an effective field-of-view of approximately 300 km^2 . Measurements were made for almost half a martian year, with winter and spring in the northern hemisphere and summer and fall in the southern hemisphere. The detectability limit of the spectrometer was approximately 3 $\mu\text{m-atm}$ of ozone. The process used by earlier investigators to extract the ozone abundance from the observed Mariner 9 spectra is as follows [1]. Each spectrum was filtered to remove spurious data points, then compared to the solar flux spectrum and shifted slightly in wavelength in order to compensate for any systematic shift in the wavelength calibration of the spectrometer. Incoming solar radiation was assumed to undergo Rayleigh scattering by CO_2 and Mie scattering by the polar hood, and to be

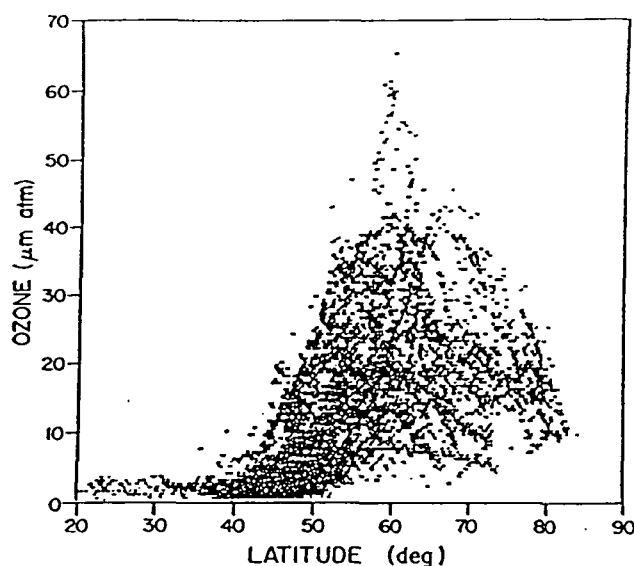


Fig. 1. Measurements of the O_3 column abundance inferred from the Mariner 9 UV spectrometer data during the northern winter, $L_s = 330$ – 360 , in the northern hemisphere (see [2]).

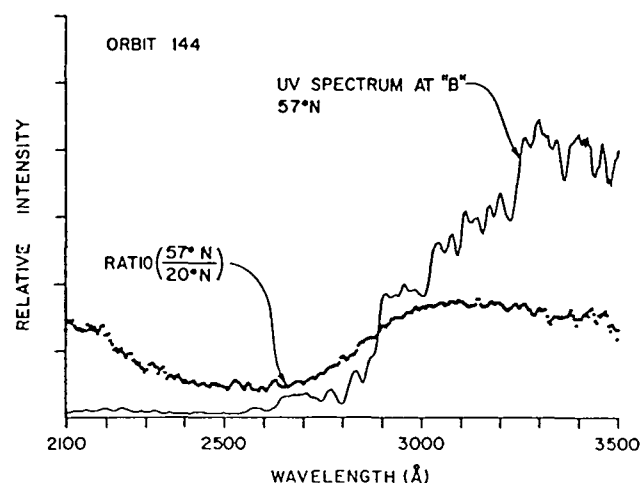


Fig. 2. Ultraviolet spectrum measured by Mariner 9 at 57N latitude on orbit 144. To enhance the O_3 absorption feature, this spectrum was divided by one obtained at 20N latitude on orbit 144, where O_3 abundances are minimal [1].

reflected by a wavelength-independent surface albedo. The only atmospheric absorption in the 2000- to 3000-Å region was assumed to come from the Hartley band system of ozone, and therefore the amount of ozone was inferred by fitting this absorption feature with laboratory data of ozone absorption, as shown in Fig. 2. O_3 absorption of sunlight is not strong enough to affect atmospheric temperature on Mars [3], and hence cannot be inferred from temperature measurements.

I use a radiative transfer model based on the discrete ordinate method to calculate synthetic radiance spectra. Figure 3 shows that when typical amounts of dust and cloud are present, significant underestimation of O_3 occurs. A factor of 3 times as much O_3 is needed to generate the same spectrum as for a clear atmosphere. If

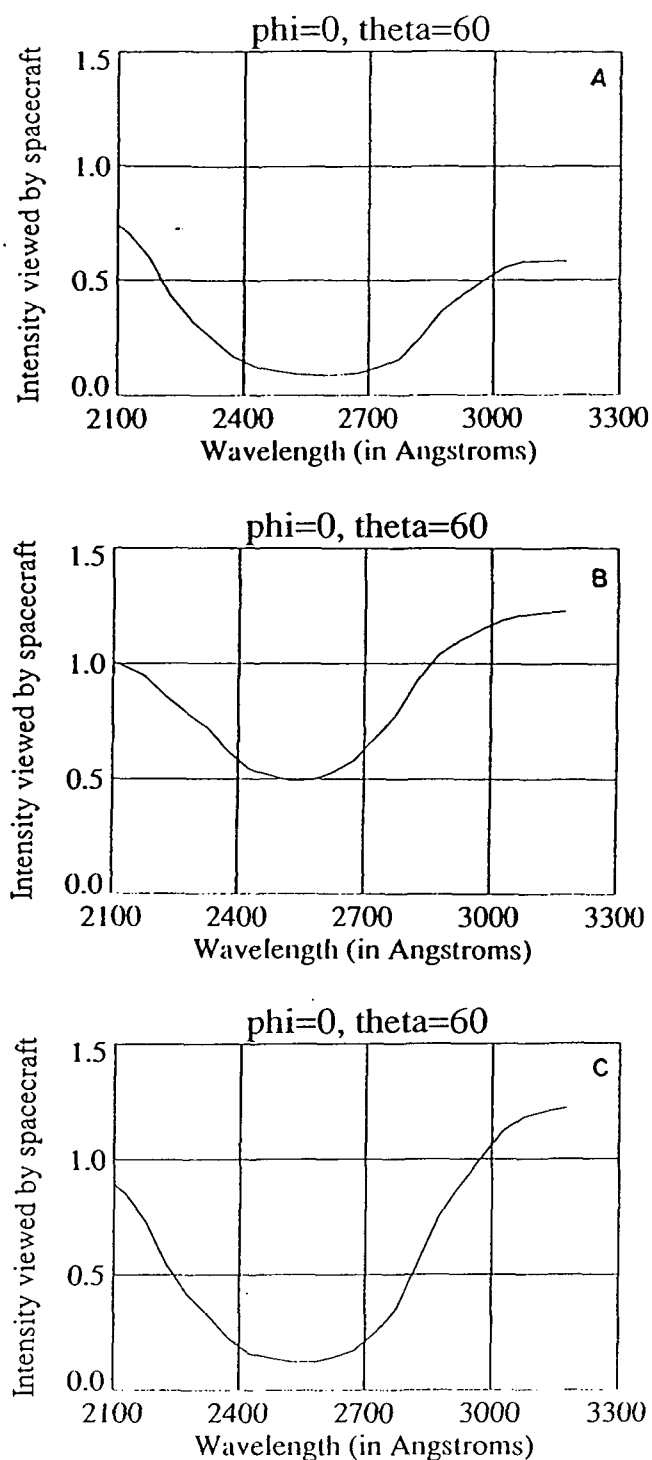


Fig. 3. Synthetic spectra as would be observed by spacecraft for atmospheres with (a) no cloud or dust and 30 mm-atm O_3 , (b) vertical opacities of dust and cloud of 0.3 and 1.0 respectively and 30 mm-atm of O_3 , and (c) vertical opacities of dust and cloud of 0.3 and 1.0 respectively and 100 mm-atm of O_3 . All cases assume a solar zenith angle of 75 (typical for winter polar observations) and viewing angle of 60, with azimuth angle of 0 (typical for Mariner 9). Polar cap albedo of 0.6.

the scattering properties of martian clouds and dust were well known, then their appearance would not be a problem, as a model would be capable of retrieving the O_3 abundance. However, these properties are not well known, which raises doubts about the effectiveness of the current UV spectroscopy technique used to measure O_3 .

Spatial and temporal variability in temperature and water vapor have been claimed to account for the scatter of the data points in Fig. 1 [4]. A decrease in temperature would result in a decrease in water vapor, if saturated as expected at prevalent temperatures. A decreased water vapor abundance decreases the availability of odd hydrogen, which converts CO and O into CO_2 catalytically, decreasing the abundance of O needed to form O_3 . However, water vapor is a small source of odd hydrogen in the winter polar atmosphere, and may not account for most of the variability in Fig. 1 [5]. Masking by clouds and dust may also account for some of the observed O_3 variability, because the nature and opacity of the clouds and dust in the polar hood change dramatically in latitude and even on a day-to-day basis. As the maximum O_3 abundance resides near the surface [5], spacecraft must be able to observe through the entire cloud and dust abundance in order to actually see the total O_3 column abundance. If reflectance spectroscopy is used, as on Mariner 9, then the cloud and the airborne dust must be traversed twice, first by the incoming solar flux down to the surface and then once again upon reflection from the surface out to the spacecraft. In addition, the large solar zenith angles at winter polar latitudes mean several times the vertical opacity of cloud and dust must be traversed. Indeed, part of the observed latitudinal variation in O_3 in Fig. 1 may be due to the inability of the spacecraft to observe through the increasing effective optical depths as one goes poleward.

The UV spectrometer on Mariner 9 was incapable of penetrating the dust during dust storms [1]; the single-scattering albedo and phase function of airborne dust and cloud ice are not known to the degree required to extract the small UV signal reflected up from near the surface. The reflectance spectroscopy technique would also have difficulty detecting the total column abundance of O_3 in cases where large dust abundances exist together with the polar hood, especially at high latitudes where large solar zenith angles magnify those optical depths; yet these cases would contain the maximum O_3 based on theoretical results [5]. It is quite possible that the maximum O_3 column abundance observed by Mariner 9 of 60 $\mu\text{m-atm}$ is common. In fact, larger quantities may exist in some of the colder areas with optically thick clouds and dust. As the Viking period often had more atmospheric dust loading than did that of Mariner 9, the reflectance spectroscopy technique may even have been incapable of detecting the entire O_3 column abundance during much of the Mars year that Viking observed, particularly at high latitudes.

Acknowledgments: I acknowledge support under contract NASW-4614.

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N94-22434

IN SITU IDENTIFICATION OF THE MARTIAN SURFACE MATERIAL AND ITS INTERACTION WITH THE MARTIAN ATMOSPHERE USING DTA/GC. R. L. Mancinelli and M. R. White, NASA Ames Research Center, Moffett Field CA 94053, USA.

Little is known about the mineralogy of the martian surface material. Several techniques have been suggested as candidates for the *in situ* identification of the martian surface material. The most promising of these techniques include differential thermal analysis (DTA) coupled with gas chromatography (GC) and differential scanning calorimetry (DSC) coupled with either mass spectrometry (MS) or GC. Our studies have shown that differential thermal analysis coupled with gas chromatography (DTA/GC) is a more appropriate analytical technique than DSC/MS or DSC/GC to identify the mineralogy of the martian surface material *in situ* [1]. DTA/GC can be regarded as an advancement from pyrolytic GC analyses that have been successfully flown on previous missions, but have supplied only limited mineralogical information [2].

Coupling a DTA with a GC enables one to identify and quantify gases that evolve during the heating process (e.g., organics, CO₂, H₂O, etc.), and allows one to correlate the thermal events on the DTA with the specific gases evolved during that event. This allows one to characterize samples. This characterization allows the distinction to be made among a variety of mineral classes (e.g., clays, zeolites, and silicates, degrees of hydration, CO₃²⁻, NO₃⁻, etc.).

The development of a prototype flight instrument is based upon criteria developed using laboratory equipment. To define the flight experiment, laboratory analyses were conducted using a Dupont model 1600 high-temperature DTA oven equipped with a model 910 cell base. Typically, 30 mg of sample was analyzed and 30 mg of Al₂O₃ served as the reference. The chamber was sealed, and the analysis performed under a vacuum. The system is controlled by a Sun Sparc II workstation. The interface between the DTA and the GC consists of a stainless steel tube, equipped with pressure sensors, leading to the GC sampling valve. If during the heating process gas evolves, it is sensed by the pressure sensors, which trigger a valve allowing the gas to be expanded from the oven chamber into a GC sample loop for GC analysis. The Sun then automatically injects the sample onto the GC column and resets the system for another event.

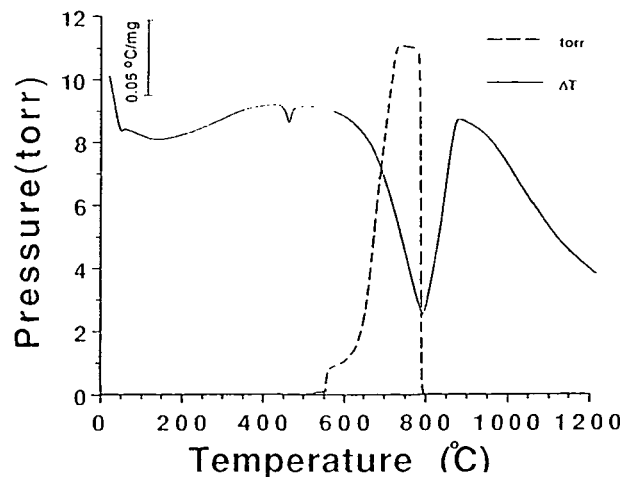


Fig. 1. DTA signature and concomitant pressure sensor readings for the analysis of an evaporite from Yellowstone National Park, Wyoming.

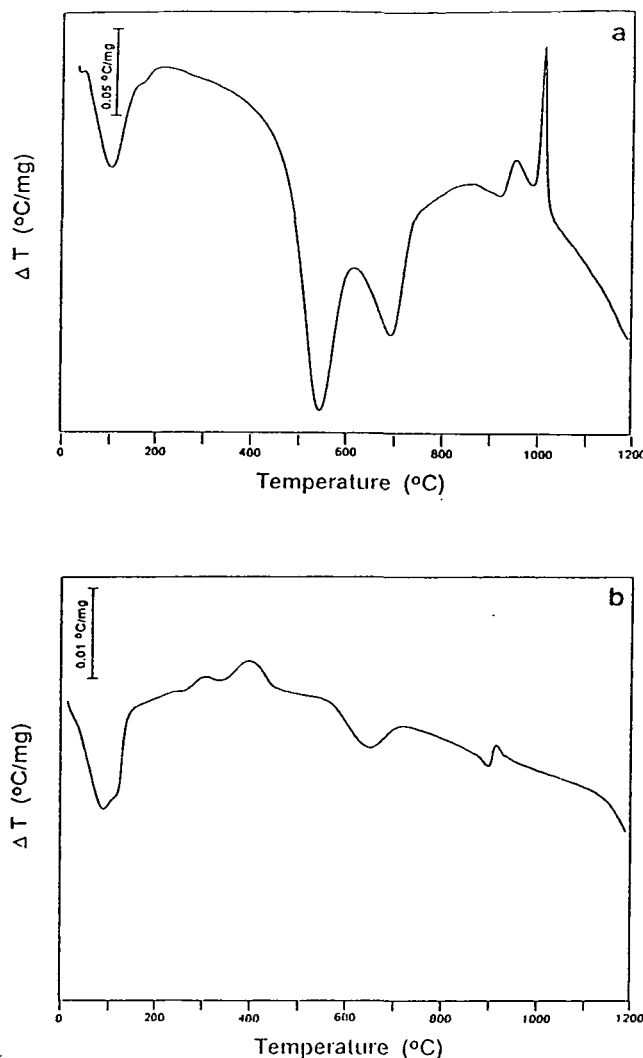


Fig. 2. DTA signatures for (a) a 1:1 mixture of montmorillonite and kaolinite and (b) Fe-enriched montmorillonite.

When a gas is evolved during a thermophysical event, the temperature is recorded such that the evolved gas is temperature-stamped so it can be associated with a specific thermal event to the nearest degree. For example, the analysis of an evaporite collected from Yellowstone National Park, Wyoming, reveals that at ~800°C an endotherm occurs that is associated with the release of a gas (Fig. 1), identified as CO₂. The sample identification software yields an identification of the sample and the probability of its accuracy. For this analysis the sample was identified as aragonite and calcite with a probability of 99%.

Because it has been suggested that clays may be an important component of the surface of Mars [4], their identification during *in situ* experiments will be important. Examination of the DTA signature for a 1:1 mixture of Crook County, Wyoming, montmorillonite and kaolinite from Washington County, Georgia, (KGa-1) (Fig. 2a) reveals that the two clays can be easily distinguished by their dehydroxylation exotherms (550°C for kaolinite and 700°C for montmorillonite) and high-temperature transition exotherms (970°C for montmorillonite and 1020°C for kaolinite). The difference in the high-temperature transition is key in distinguishing a variety of clays

from each other using the DTA. Figure 2b depicts Fe-enriched montmorillonite clay prepared by the procedure of Banin et al. [3,4]. The endotherm occurring at 280°C is due to the dehydroxylation of lepidocrocite ($\gamma\text{-FeOOH}$) to $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) and is accompanied by dehydroxylation and the formation of H_2O vapor. The exothermic peaks observed at 321°C, 430°C, and 590°C are due to the transition of $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$ (hematite). The differences in temperature are due to particle size differences. In general, the limit of detectability for a mineral or organic compound in the DTA is ~1% (wt/wt) [5].

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ATMOSPHERIC IMAGING FROM MARS LANDED STATIONS. Terry Z. Martin, Jet Propulsion Laboratory, Mail Stop 169-237, 4800 Oak Grove Drive, Pasadena CA 91109, USA.

A wide variety of information about atmospheric phenomena at the surface of Mars can be obtained with imaging systems on landed stations. I discuss here the range of such observations and their requirements.

Atmospheric Opacity: Determination and History: Dust opacity is central to the meteorology of Mars through its effect on the absorption of sunlight. This parameter may be used, as with Viking Lander imaging data, to infer global behavior, although we know that there are strong areal variations in the distribution of dust and ice clouds. The opacity indicates the effect of dust storms and the column abundance of one form of water, given separation of dust from ice opacity by diurnal variation or filter capability.

Determination of opacity can be done with very simple optical detectors such as a diode and a hemispheric window. However, given an imaging system, the problem is that of imaging the Sun (or Phobos, or a star) directly, or a calibration target illuminated by the Sun. Nighttime opacity measurements can be particularly important for fog detection and studying dust settling. Calibration targets are not ideal for opacity measurement because they can collect dust when oriented upward.

The frequency of measurement for opacity depends on the causal mechanism. Local dust storms can raise dust in minutes; it would be of great value to observe this phase from a lander. High-frequency observations can be triggered by other data, like wind speed. Global storms would cause much slower changes, so that daily measurements might suffice. Water ice variations seem to be diurnally induced, indicating hourly observations.

Atmospheric Aerosols: Physical Properties: Greater angular resolution allows going beyond total optical depth to obtain information about the size and distribution of airborne particles; the information is contained in the scattering phase function. The sky brightness should be measured as a function of distance from the solar disk, with an accuracy and resolution of about 1°. For phase function measurement, there is much redundancy in an image of the sky. A parameterization of the intensity contours of an image would be adequate if internal instrument scattering effects can be removed.

Separation of the dust and ice components of the atmosphere can be done by observing diurnal variation of the scattering behavior and using a variety of spectral filters.

Observations of the sky near sunrise and sunset can provide unique information about the vertical distribution of particulate matter, since the sunlight's path is constrained by the planet's edge. The increased path to the Sun through the atmosphere also serves to magnify color effects produced by particulates.

Clouds: Detection and Tracking: Individual clouds are common in orbital images of Mars; these arise from topographic or polar edge effects, from regional circulation behavior, or local turbulent phenomena such as dust devils. CO_2 ice clouds in the winter polar caps are also inferred from IR measurements. Stations on the martian surface offer unique opportunities to observe these clouds: The observing site is fixed and chosen; the spatial scale is small; and the geometry is unique.

A fixed observing site means that an individual cloud can be tracked over a longer period of time than a typical orbiter can devote (although both approaches are desirable). Clouds, of course, act as wind indicators, including winds at levels the lander cannot sample directly. A site can, in principle, be chosen partly for the cloud phenomena known to be found there (fogs, lee wave clouds, dust activity). The landed station can observe phenomena that would be too small to discern in large-scale imaging data: dust devils, other gust-induced dust storms, and small fog banks. Finally, the lander geometry provides observation at high phase angles that are especially suitable for detection of thin clouds. The depth of fogs can be established far more easily from a lander than from orbital altitudes.

It should be mentioned that one particular observation mode employed by the Viking cameras, in which the same vertical line was repeatedly scanned, has special value for atmospheric observations. Clouds passing through the field, as well as the changing brightness of the sky as the Sun moves, can be recorded. This mode of observation is relatively conservative of data rate.

It seems particularly appropriate for a mission addressing meteorology that the surface stations, spread widely over the surface, also devote time to looking directly at the atmosphere. The synergism possible is important. For example, consider the value of imaging observations triggered by detection of wind gusts that might raise dust locally. Similarly, recording could be stimulated by a hygrometer's indication of the presence of fog.

It is also possible for atmospheric imaging to affect the course of other investigations. The presence of clouds can alter the color of rocks. Cloud motions can corroborate wind measurements. Opacity data can influence the choice of times to collect samples (to avoid or select dust deposition effects).

One particularly interesting case of surface and atmospheric objectives coming together is the observation of small-scale wind streaks—surface phenomena caused by the wind. There is every reason to believe that scouring and deposition act on the small scale seen by a landed station, as well as on the familiar large scale. Locating a station in an area known to experience large seasonal changes would open up the possibility of measuring the characteristics of blowing dust, thus corroborating the models built up over many years by Greeley and coworkers.

An all-sky camera would ideally satisfy atmospheric science objectives. However, a camera designed for surface science will also be of value for atmospheric science if it can (1) point above the horizon (minimum requirement); (2) sample phase angles approaching 180° (better); (3) point at the Sun (best); (4) remove internal scattered light effects through calibration; (5) provide images over a range of visible band wavelengths; or (6) provide sensitivity adequate to image Phobos or bright stars.

N94-22435

MASS SPECTROMETER-PYROLYSIS EXPERIMENT FOR ATMOSPHERIC AND SOIL SAMPLE ANALYSIS ON THE SURFACE OF MARS. Konrad Mauersberger¹, Paul Mahaffy², and Hasso Niemann², ¹School of Physics and Astronomy, University of Minnesota, 116 Church St. S.E., Minneapolis MN 55455, USA, ²Code 915, NASA Goddard Space Flight Center, Greenbelt MD 20771, USA.

Introduction: Results from the Viking mission will form the foundation for future in-depth investigations of atmosphere-surface interactions on Mars. The two Viking landers carried impressive instrumentation to obtain and analyze soil samples: The sites were observed by cameras, and the collector head was located on a long boom and allowed the collection of large samples at various depths. A selection of grain sizes was possible and a distribution system supplied a number of experiments with soil material. Despite stationary vehicles, a wide sampling field was reachable. The GCMS system, responsible for atmospheric as well as surface soil analysis, worked well on both landers. Atmospheric measurements resulted in the determination of the abundance of noble gases as well as of other molecular species. Isotopic composition measurements included the important ratios of ¹³C/¹²C, ¹⁵N/¹⁴N, and ³⁶Ar/⁴⁰Ar. To verify these past results and to advance detailed studies of noble gas isotope ratios and minor constituents, better instrument sensitivities, higher precision, and lower background contributions are required in future Mars missions. Soil analysis during the Viking mission concentrated on organic material. Heating cycles were performed to 500°C and only water and carbon dioxide were identified. Higher pyrolysis temperatures are of primary importance to advance our understanding of the mineralogy and gas loading of surface material and atmospheric exchange.

Objectives: An experiment is under development that will combine atmospheric gas analysis with the pyrolysis of collected soil samples. This paper will focus on the pyrolysis part of the experiment. The design has been guided by the following assumptions: (1) The system must have the capability for multisample analysis, (2) the temperature range must exceed 500°C and should reach 1000°C by using an efficient heating system, and (3) the pyrolysis system with analyzer must be small in size and mass in order to be considered for a number of future Mars missions.

One of the important science objectives will be the search, performed by studying characteristic release patterns during heating, for specific mineral types such as carbonates or sulfates. Within the temperature range of the pyrolysis process of approximately 1000°C nitrates should be released between 300°C and 400°C as NO₂, carbonates near 500°C to 600°C as CO₂, and, finally, sulfates will decompose into SO₂, H₂S, or others between 800°C and 1000°C. Isotope ratios of C, O, and S will be determined as the molecules carrying these elements appear in the mass spectrum.

While a gas chromatograph ahead of the mass spectrometer may provide a useful separation of complex organics, the proposed stepwise heating system of the pyrolysis experiment and the expected low abundance of organic compounds does not justify the additional complexity of a gas chromatograph at the present time. A mass spectrometer can quickly scan a large mass range to survey released gases including their time evolution during the pyrolysis process. In addition, isotope ratios can be measured and enrichment procedures can be monitored and the products analyzed.

Experiment Description: The present design of the pyrolysis experiment is based on a small cylindrical unit (~300 cc) that contains a rotatable disc where 6–8 cells (or crucibles) are located on its periphery. Each cell is made of sapphire and can accept about

2 cc of soil material. In order to load a cell, it is rotated under an opening on top of the cylinder, and thereafter is placed into a stationary oven to start the pyrolysis process. The heating will proceed in a stepwise or ramp fashion. Assuming each cell is loaded to about one-half or one-third of its capacity, repeated use of a cell after the first pyrolysis process (and some additional heating) is possible.

The evolved gas will be fed into the mass spectrometer, which will also be used for atmospheric gas analysis. The small quadrupole gas analyzer has been employed in many previous space experiments and is characterized by both a high sensitivity and mass resolution.

Discussion: On a broader scale, the pyrolysis experiment actually contains a number of subsystems that must also be considered for a space mission. The parts may be subdivided into sample collector, sample transfer to pyrolysis cells, pyrolyzer, pumping system, gas transfer, and gas analyzer.

The first two subsystems are difficult to evaluate at the present time. They depend strongly on the spacecraft configuration and on the support provided to experiments. On a mission with small spacecrafts, sample collection and transfer may become a difficult task. The pyrolysis experiment sketched above was initially designed for a rover containing a sample collector and distributor for onboard experiments.

The pumping system plays a central role in the operation of the pyrolysis system and mass spectrometer. In the past, getter and sputter ion pumps have been used in space missions to evacuate gas transfer and mass spectrometer systems. Those pumps, however, may cause interferences with noble gases by outgassing previously pumped material or by introducing pumping speed-dependent enrichments or depletions. To circumvent those deficiencies, development of a turbomolecular pump has been initiated that will be capable of operating against the martian atmospheric pressure yet maintaining ultrahigh vacuum conditions inside the attached instruments. With a mass of about 1 kg and a power consumption of 12 W, pumping speeds of 10 to 50 l/s should be achieved. Even when adding the required robustness of space flight equipment, present technology makes the development of such a small pump feasible.

In summary, a combination of a flight-proven mass spectrometer with noble gas enrichment cells, a lightweight, low-power turbomolecular pump, and a multicell, high-temperature pyrolysis system are under development that could provide the next generation of atmosphere-surface analysis instruments after the Viking mission.

N94-22436

TEMPERATURE/PRESSURE AND WATER VAPOR SOUNDING WITH MICROWAVE SPECTROSCOPY. D. O. Muhleman¹, M. A. Janssen², R. T. Clancy³, M. Frerking², S. Gulkis², D. J. McCleese², R. Zurek², and R. M. Haberle⁴, ¹California Institute of Technology, Pasadena CA 91125, USA, ²Jet Propulsion Lab, 4800 Oak Grove Drive, Pasadena CA 91109, USA, ³LASP, Washington University, St. Louis MO 63130, USA, ⁴NASA Ames Research Center, Moffett Field CA 94035, USA.

Two intense microwave spectral lines exist in the martian atmosphere that allow unique sounding capabilities: water vapor at 183 GHz and the (2-1) rotational line of CO at 230 GHz. Microwave spectral line sounding is a well-developed technique for the Earth's atmosphere for sounding from above from spacecraft and airplanes, and from below from fixed surface sites. Here we describe two simple instruments for temperature sounding on Mars (the CO line) and water vapor measurements. The surface sounder proposed for the MESUR sites is designed to study the boundary layer water vapor

distribution and the temperature/pressure profiles with vertical resolution of 0.25 km up to 1 km with reduced resolution above approaching a scale height. The water channel will be sensitive to a few tenths of a micrometer of water and the temperature profile will be retrieved to an accuracy between 1 and 2 K. The latter is routinely done on the Earth using oxygen lines near 60 GHz. The measurements are done with a single-channel heterodyne receiver looking into a 10-cm mirror that is scanned through a range of elevation angles plus a target load. The frequency of the receiver is sweep across the water and CO lines generating the two spectra at about 1-hr intervals throughout the mission. The mass and power for the proposed instrument are 2 kg and 5–8 W continuously. The measurements are completely immune to the atmospheric dust and ice particle loads. We feel that these measurements are the ultimate ones to properly study the martian boundary layer from the surface to a few kilometers. Sounding from above requires an orbiting spacecraft with multichannel microwave spectrometers such as the instrument proposed for MO by a subset of the authors, a putative MESUR orbiter, and a proposed Discovery mission called MOES (Sanjay Limaye, PI). Such an instrument can be built with less than 10 kg and use less than 15 W. The obvious advantage of this approach is that the entire atmosphere can be sounded for temperature and water vapor in a few hours with somewhat better than a scale height resolution. If a bigger mirror is used (>30 cm) limb sounding geometry can be employed and half scale height resolution achieved to altitudes up to at least 60 km. Again, the measurements are immune to dust and ice loads. Water vapor sensitivity of 0.1 μm can be achieved (even with a nadir instrument) and temperature profiles retrieved to an accuracy of better than 2 K from the surface to about 60 km. Winds can be measured from the doppler shifts of CO lines in the limb sounding mode.

PRELIMINARY EXPERIMENTAL RESULTS OF UV IRRADIATION OF CARBONATES. L. M. Mukhin¹, J. Huth¹, H. Wänke¹, Y. Dikov², and A. P. Koscheyev³, ¹Max-Planck-Institut für Chemie, Mainz, Germany, ²IGEM, Moscow, Russia, ³Karpov Institute of Physical Chemistry, Moscow, Russia.

The data on the chemical composition of the martian surface and atmosphere and the intensity and spectral distribution of solar irradiation at the surface of Mars lead to the suggestion that photochemical processes can play a significant role in the chemical evolution of the martian atmosphere and surface. In a number of experimental papers the potential importance of gas-solid photochemistry for the chemical evolution of the martian atmosphere and surface has been shown [1–5]. However, there is a lack of information about the stability of native minerals under UV irradiation. This problem is important for Mars because the surface of this planet is open for short wavelength UV with $\lambda > 190$ nm. In the present work we investigated the stability of calcite under UV irradiation. Our experimental set-up is schematically represented in Fig. 1.

The sample of calcite monocrystal with a geometrical surface area of ≈ 1 cm² was mounted in a vacuum chamber with a sapphire window, transparent to UV irradiation with $\lambda > 180$ nm. Prior to UV irradiation the total pressure in the chamber was higher than 10^{-7} mbar. The surface of the sample was exposed to UV irradiation using a 30-W deuterium lamp.

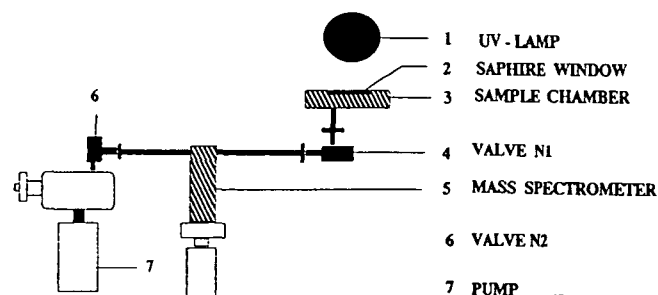


Fig. 1.

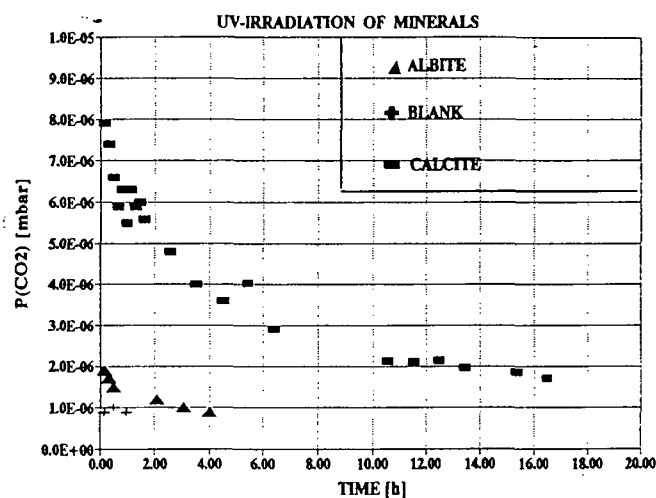


Fig. 2.

In typical runs the sample was exposed to UV irradiation for about 20 hr. Once every hour the chamber was closed by valve N1 (Fig. 1) and after 10 min exposition the gas composition in the chamber was measured by a quadrupole mass spectrometer (Balzers Quadrupole mass spectrometer QMG 64), valve N1 open, valve N2 closed.

This experimental procedure allowed us to obtain quantitative data about the partial pressure of a definite gas component, especially of CO₂. In blank experiments the same procedure was used without a sample as well as with an albite sample.

The effect of evolving CO₂ from calcite under UV irradiation was detected (Fig. 2). The possible explanation of this effect is the photodestruction of calcite under UV irradiation. If the evolving CO₂ is really connected with the photodestruction of carbonate, then a simple estimation shows that the rate of photodestruction is equal to 2.5×10^{-4} nm/s. The blank experiment did not show noticeable CO₂ production. The possible application of this effect to martian conditions needs more detailed investigations.

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COMPAS: COMPOSITIONAL MINERALOGY PHOTOACOUSTIC SPECTROMETER. W. Hayden Smith, Washington University, St. Louis MO 63130, USA.

Science Objectives: Chemical and mineralogical compositions are key data needed for reconstruction of the development history of the martian crust and of the soils that cover it. Photochemical weathering is an active, important process on Mars, controlling the nature of exposed rock surfaces. It is necessary to differentiate the surface weathering products from the underlying base rock. The weathering process itself is an important consequence of the atmosphere-surface interaction, about which we know little [1]. The surface patina provides the means to characterize the weathering process. Penetration of the surface patina is necessary to characterize the underlying base rock.

Measurement Objectives: There is a critical need for a true absorption spectroscopic method for *in situ* rock studies to complement remote sensing by diffuse reflectance spectroscopy. The absorption spectra that are independent of the spectral effects of scattering, particle size, and distribution provide accurate and reliable diagnostics of rock species. Such a method would be invaluable for detailed rock-level mineralogy during martian micro- and minirover missions. Mineralogical knowledge complements elemental data and the visible and infrared spectra provide invaluable information about the texture of the materials on the martian surface and about the nature of the weathering processes that have occurred. Gamma ray measurements from martian orbit suggest that the chemical signature of the surface is dominated by materials similar in composition to the materials analyzed at the Viking sites, i.e., of basaltic affinities [2]. Mars Observer is scheduled to begin mapping operations late in 1993 and includes a gamma ray spectrometer to map surface chemistry and a thermal emission spectrometer (TES) to delineate mineralogy and surface texture [3]. A problem that will

be faced in the analysis of TES data is the ubiquitous presence of soils and rock coatings (e.g., [4]). It will be difficult to separate the portion of the emission signal coming from weathering products from the portion arising from emission of relatively fresh bedrock. An important use of COMPAS would be to clarify and confirm global measurements by Mars Observer by characterizations at the rock level of rock coatings and unweathered rock surfaces. This task can only be accomplished at the rock scale. The results will address the fundamental questions of what dominant rock types are exposed at the surface and the nature of the surface-atmosphere interaction.

Measurement Approach: We plan to develop and demonstrate COMPAS, the Compositional Mineralogy Photoacoustic Spectrometer, for *in situ* spectral characterization of rocks and their surface weathering products and/or the nature of adsorbed species. Photoacoustic spectroscopy (PAS) is an established technique that has been widely applied in spectral studies of complex, highly light scattering, unprepared opaque samples. Existing PAS studies include rock and mineral characterizations and kinetic studies of the same surface chemical reactions expected in photochemical weathering processes at the martian surface.

Microminiaturization of COMPAS to ensure compatibility with simple microrovers is feasible. Our design goals for COMPAS are volume < 125 cm³, weight < 110 g, and power consumption < 1.5 W. The no-moving-parts COMPAS acquires single-point spectral data serially at a modest data rate, compatible with microrover capabilities. COMPAS will measure spectra over at least 0.7-2.7 μ m, the prime spectral band for mineralogy and water detection for martian environment surface studies. Subsequently we will define COMPAS for extensions to both shorter and longer wavelengths. Since COMPAS incorporates a thermal detector, the capability to sense an extremely broad range of wavelengths is feasible so that rock types can be measured at the wavelengths that yield optimum sensitivity or minimum interference for the rock studied. COMPAS can acquire spectra from the UV to the far-IR to study rocks, surface weathered components, and adsorbed species. COMPAS can also profile surface layers to depths as great as 1 mm by using the variation of absorption coefficients and the modulation frequency used in the measurement. Then the depth profile of weathered samples can be measured accurately to determine exposure ages.

PAS differs from conventional reflectance spectrometry in that it uses the sample as the detector. Diffuse reflectance spectrometers compare the reflectance of the sample with that of a standard so that the difference between two quantities is measured. If the absorption is large, little light is returned, or if small, only scattered light is observed. In contrast, PAS senses only the effects on the sample of the absorbed light and produces an "emissionlike" spectrum that is entirely equivalent to the true absorption spectrum. The sample responds to a modulated input flux by an expansion and contraction that may be detected as an acoustic wave carried by the CO₂ atmosphere of Mars. Since the pressure wave or the acoustic wave is induced by the periodic temperature modulation in the rock induced by the modulated absorption of incident light converted into heat, scattered light has little effect on PAS.

COMPAS collects sunlight with a nontracked collector (either aspheric or reflective) over ± 3 hr from zenith and focuses it into a fiber optic. The fiber optic transmits the flux to an acoustic-optic tunable filter (AOTF) used to control and modulate the flux reaching the sample. The AOTF output is collected by fiber optics and illuminates the rock surface. The AOTF offers high transmission

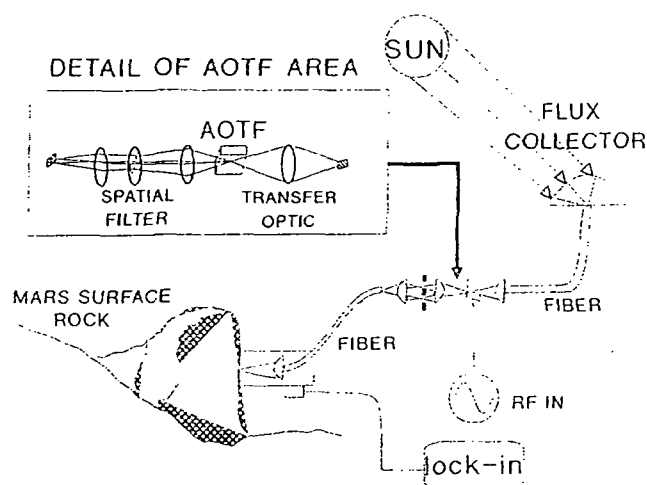


Fig. 1.

(>75%), adaptable spectral resolution, an arbitrarily selectable spectral pass band, adaptable pass band shape, and high time resolution as a shutter or light modulator, all under electronic control (see [6,7]).

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OPTICAL LUMINESCENCE SPECTROSCOPY AS A PROBE OF THE SURFACE MINERALOGY OF MARS. A. H. Treiman, NRC Associate, Code SN4, NASA Johnson Space Center, Houston TX 77058, USA.

Executive Summary: Optical luminescence (OpL) spectroscopy is an attractive use of a visible-near-IR spectrometer on a Mars lander because mineral products of atmosphere-surface interactions on Mars will probably have characteristic OpL spectra. Optical luminescence spectra would be taken at night, when a spectrometer might otherwise sit idle. Also needed would be a source of exciting radiation, which could be shared with other experiments.

Optical luminescence is emission of nonthermal optical photons (near-UV through near-IR) as a response to energy input [1–3]. On absorption of energy, an atom (or ion) will enter an excited state. The favored decay of many such excited states involving valence-band electrons is emission of an optical photon. Optical luminescence spectra can be useful in determining mineralogy and mineral compositions.

Optical luminescence in crystals can arise from essential elements (or ions), trace-element substituents (activators), or defects. Common activators in salts of alkali and alkaline earth elements include $Mn^{2+}(VI)$, other transition metals, the rare earths, and the actinides [3]. Trace substituents of other species can enhance or quench OpL (e.g., Pb^{2+} vs. Fe^{3+}). Optical luminescence can also arise from defects in crystal structures, including those caused by radiation and shock.

Optical Luminescence on Mars: Atmosphere-surface interactions on Mars may yield many luminescent minerals, notably salts of the alkali and alkaline earth elements [4–6]. Such phases are products of martian weathering in the SNC meteorites [7–10], and some do exhibit OpL. Scapolite has unusual OpL (Fig. 1), and any scapolite on the Mars surface [11] should be readily apparent through OpL spectrometry.

Luminescent minerals may be more common on Mars than Earth. Martian surface materials are likely to have suffered significant radiation damage from cosmic rays, which may create luminescent defect structures. Some OpL mechanisms will be enhanced in the cold of the martian night.

Optical Luminescence Excitation on Mars: To permit OpL spectroscopy, a Mars lander must have an energy source for OpL excitation, such as UV light, high-energy electrons, or heat.

Optical luminescence from UV light usually uses a Hg gas lamp, an “off-the-shelf” technology that would draw moderate power. However, Hg lamps may be fragile and are not very bright, thus requiring that samples be brought to the spectrometer. Use of a UV laser would resolve these problems and permit other laser-based

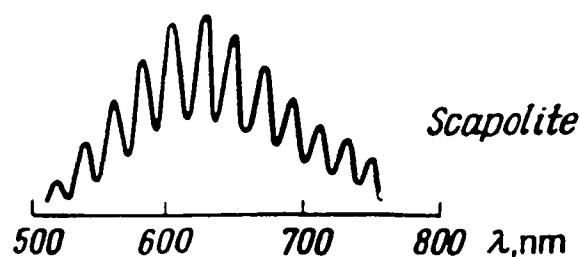


Fig. 1. OpL spectrum of scapolite containing S_2^{2-} . Scapolite formed in an oxidizing environment will have a similar spectrum [2].

experiments (atmospheric OpL and scattering, distance ranging). However, UV lasers commonly use gas or liquid media; solid-medium UV lasers are under development.

Optical luminescence excited by electron flux, cathodoluminescence (CL), is commonly used in geological sciences [12]. Cathodoluminescence yields the brightest luminescence of available methods, uses “off-the-shelf” technology, can work in ambient Mars atmosphere (penetration to tens of centimeters), and produces characteristic X-rays (which may permit determination of chemical compositions). However, CL would require a source of 10–15-kV electrons, significant power resources, and transport of samples to the spectrometer.

Optical luminescence emitted during heating, thermoluminescence (TL), is a standard technique in meteorite and radiation studies. Thermoluminescence can be readily related to radiation exposure, and a suitable heating chamber (like a TAPS calorimeter) may be available on the lander. However, TL requires samples to be within the lander, and does not utilize the wide range of activation mechanisms tapped by CL and OpL methods.

Conclusion: Optical luminescence spectrometry could provide important and cost-effective constraints on the surface mineralogy. It could utilize a visible-NIR spectrometer during the times it would otherwise be idle. The excitation source for OpL could be shared with other science experiments, including atmosphere monitoring, calorimetry, or bulk chemical analyses.

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MÖSSBAUER SPECTROSCOPY ON MARS: WHAT TO EXPECT. L. Vistisen¹ and J. M. Knudsen², ¹Niels Bohr Institute, Blegdamsvej 17, DK-2100, Copenhagen Ø, Denmark, ²Physics Laboratory, H.C. Ørsted Institute, Universitetsparken 5, DK-2100, Copenhagen Ø, Denmark.

Mössbauer spectroscopy is one of the most versatile tools for the study of the physics and chemistry of iron compounds. Through this simple technique information can be obtained on the oxidation state of the iron and the distribution of the element on the various accessible lattice sites in crystals. Mössbauer spectroscopy also gives unique information on magnetic properties of compounds, be they ferro-, ferri-, or antiferro-magnetic. In the study of superparamagnetism the technique is indispensable. The main objective of the present paper is to show a few Mössbauer spectra of Mars sample analogues and SNC meteorites. These spectra will suggest what might be achieved by performing Mössbauer spectroscopy on the surface of Mars.

Experimental: The spectra are recorded in backscatter geometry with no sample preparation, which is the method planned for Mössbauer spectroscopy on Mars. The gamma rays are counted using a silicon diode (Hamamatsu S3590-05), the ⁵⁷Co source used is about one year old, originally 100 mCi, and the drive is a conventional one, not minimized. The collimator-source geometry allows emission of gamma rays with a maximum deviation of 20° from the central axis. The recording time for the spectra shown in Fig. 1 is 24 hr, except for spectrum c1, which was recorded over 7 days. c1 is aesthetically better than c2, but the information content is nearly the same. It is expected that six detectors will be used in the instrument sent to Mars, i.e., a recording time of 4 hr will in most cases be sufficient. The results reported in this paper are obtained with drive, detector, source, and sample at a temperature of -21°C.

Examples: Spectrum a shows a clear distinction of three phases present in a terrestrial basaltic rock: magnetite, ilmenite, and olivine. The spectrum allows a quantitative determination of the distribution of the iron in the three phases identified. It should be noted that even with the described collimator-source geometry, it is possible to conclude that the magnetite contains impurities (in fact it is titanomagnetite). Spectrum b of a banded iron formation shows that hematite, seen as "shoulders" on the outer lines, is clearly distinguished from magnetite.

Soil on Mars: The martian soil is colored red by Fe(III) compounds, and during the Viking mission it was established that a ferrimagnetic phase is present in the soil. The strongly oxidizing compound in the soil, also found in the Viking mission, may be an iron mineral. Part of the Fe(III) on Mars is known to be present in small particles ($d \leq 10$ nm), probably superparamagnetic. It is thus an important problem in future missions to Mars to try to establish the Fe(III) mineralogy in the surface fines.

As analogues to the martian dust we are studying terrestrial red soils by Mössbauer spectroscopy. An example is spectrum c, which shows the presence of hematite in a sample collected from a volcano. The peaks in the middle of the spectrum show Fe(III), probably in FeOOH. By magnetic separation a few percent of the sample can be extracted, but this magnetic fraction is too small to be seen in the spectrum.

Surface Rocks on Mars: The SNC meteorites are believed to be rocks from Mars and may thus be used to anticipate what a Mössbauer spectrum of the base rocks on Mars would look like.

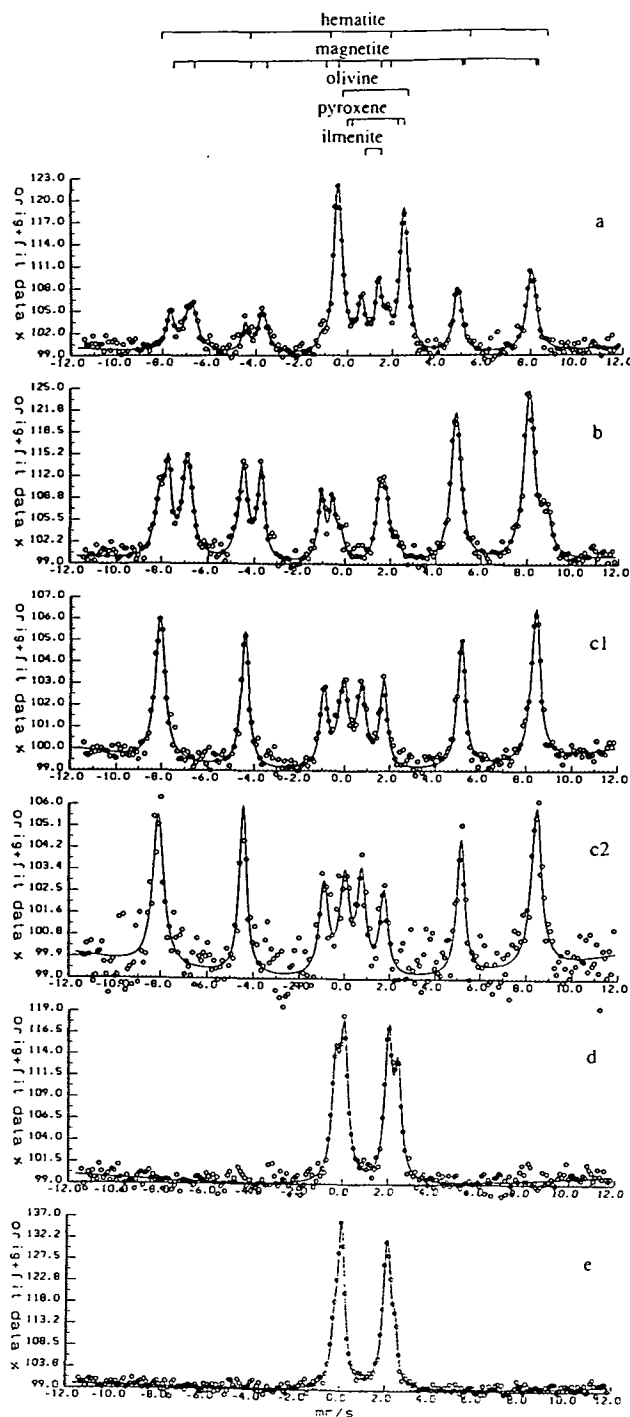


Fig. 1. Backscattering Mössbauer spectra recorded at -21°C of (a) a terrestrial basalt (Smålands Taberg, Sweden), (b) a banded iron formation (Hamersley Basin, Australia), (c) a red sample from a volcano (Santorin, Greece), c1 7 days and c2 24 hours, (d) the SNC meteorite Nakhla, and (e) the SNC meteorite Zagami.

Spectra d and e of the SNC meteorites Nakhla and Zagami show the presence of both pyroxene and olivine in Nakhla and only pyroxene in Zagami. Possible Fe(III) in these meteorites is below the detection limit of the present set-up and so is the titanomagnetite known to be present in these meteorites.

Conclusion: Through Mössbauer spectroscopy we might be able to establish (1) the identity of the main iron-containing minerals in the soil and rocks, including the determination of the fraction of iron present in a given mineral; (2) the oxidation state of the iron in the soil, i.e., the ratio Fe(II)/Fe(III); and (3) the nature of the magnetic phase in the soil, i.e., whether the phase is maghemite, magnetite, or small-sized particles of hematite.

As shown above, small amounts of magnetic phases are difficult to detect, and to fulfill the last task an adequate part of the iron must be present in the magnetic phase.

DETERMINATION OF STABLE ISOTOPIC COMPOSITIONS OF H, C, N, O, AND S AT THE MARTIAN SURFACE USING MASS SPECTROMETRY AND STEPPED COMBUSTION/PYROLYSIS. I. P. Wright¹, M. M. Grady², and C. T. Pillinger¹, ¹Department of Earth Sciences, Open University, Walton Hall, Milton Keynes MK7 6AA, UK, ²Natural History Museum, Cromwell Road, London SW7 5BD, UK.

The mechanisms by which the surface reservoirs of a planetary body interact can be assessed through an understanding of the distribution and stable isotopic compositions of the elements that constitute the reservoirs. Of particular relevance to processes that operate at planetary surfaces are the light elements: H, C, N, O, and S. Conceptually, all these can be quantified and measured for isotopic compositions using a single extraction system and mass spectrometer. Rather than carrying out physical separations of the components of interest, it is proposed that the elements under investigation are selectively removed from appropriate samples using the combined techniques of incremental pyrolysis and stepped combustion.

The chemical and physical (and biological?) processes that act on Mars will have left a record of their effects in the isotopic compositions of the different surface reservoirs (e.g., ices, fluids, gases, magmatic components, secondary minerals, etc.). Isotopic analysis of these, which will allow a reconstruction of the conditions prevailing at the time of formation, is obviously a demanding task for an instrument that needs to operate remotely and autonomously at the surface of the planet. One potentially effective technique is to use the different chemical and thermal properties of the individual constituents of interest to assist in the separation process. This can be effected to some degree by treating a multicomponent sample to a process of incremental heating (pyrolysis). A refinement of this is to perform the experiment under 0.1 bar of pure oxygen (stepped combustion). An exemplification of the value of this type of extraction can be given for the case of sulfur, where iron sulfides combust to form SO₂ at temperatures below 600°C while sulfates decrepitate to give SO₂ at temperatures in excess of 600°C. Thus, without recourse to physical separations it should be possible to make isotopic measurements of sulfur in its different redox states.

Over the years we have extensively used stepped combustion techniques and associated high-sensitivity mass spectrometers in the laboratory for determining the distribution and isotopic composi-

tions of elements such as carbon [1,2] and nitrogen [3,4]. The same procedures can also be used for hydrogen and have been attempted for sulfur [5]. All these techniques have been applied successfully to studies of SNC meteorites [6,7]. A considerable advantage of stepped combustion is that the elements of interest can still be determined even if they exist in a refractory form. This technique has even greater selectivity than simple pyrolysis and can be considered as an adjunct to any heating system that would otherwise be on the payload of a mission to Mars.

The deployment of stepped combustion for the analysis of surface materials on Mars has the following requirements: (1) Availability of a pumped, neutral mass spectrometer with a mass resolving power of ≤ 100 ; such an instrument would also be utilized for atmospheric analyses. (2) Provision of a robotic sampling device for collection and delivery of materials from the vicinity of the landing site; such a device would be common with other analytical experiments. Specific to the stepped combustion experiment would be the reaction vessel, which would need to be capable of temperature control in steps over a range from ambient to a maximum of 1200°C. Temperatures less than this value would still be informative, but the chosen maximum corresponds to that at which magmatic gases would be liberated from minerals. In order to obtain isotopic measurements of the highest precision it would be desirable to incorporate as part of the analytical instrumentation a facility to meter out small quantities of reference gas to enable *in situ* calibration of the mass spectrometer.

Much of the procedural protocol for stepped combustion has already been evaluated in the laboratory. For example, solid reagents that can supply oxygen in the gas phase at temperatures as low as 200°C are known; excess oxygen can either be vented from the system or chemically resorbed for further usage. A number of purification schemes have been advanced to allow selective admittance of a single gaseous species to the mass spectrometer (thereby avoiding isobaric interferences). In the laboratory experiments, only one gas is ever analyzed in an individual mass spectrometer. Since the instrument destined for Mars would need to be highly efficient, it would be necessary not only to purify the gases of interest (H₂, CO₂, N₂, and SO₂) but also to separate them for the purposes of sequential isotopic measurement. This could be readily achieved provided cryogenic cooling is available. An alternative would involve the use of chromatographic separation or even some form of solid-phase chemical reactions.

The concept of active chemical analysis could be adapted further for measuring the oxygen isotopic compositions of martian minerals provided that a source of fluorine can be transported to Mars. A convenient way of doing this would be to use solid K₂NiF₆·KF, which decomposes to give fluorine gas at 400°C. By reacting the fluorine with silicates, etc., it would be possible to liberate O₂ gas for analysis. In this way it would be possible to measure both ¹⁶O/¹⁸O and ¹⁶O/¹⁷O ratios.

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